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(54) Title: INSECTICIDE/FUNGICIDE INTRODUCED INTO CONTROLLED ATMOSPHERE CHAMBER
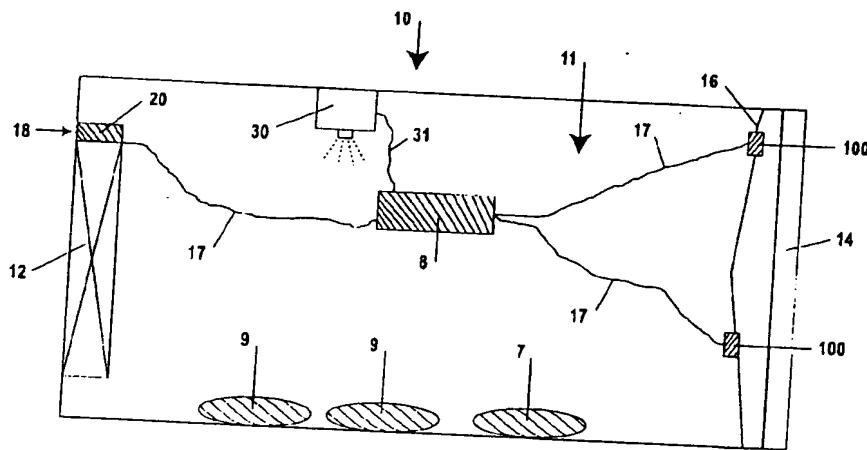
(57) Abstract: Apparatus and method for introducing one or more airborne substances such as insecticide, fungicide, fumigant or bactericide into the controlled oxygen atmosphere (11) within a chamber (10) and adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount. The substance can be carbon dioxide. The substance may be a liquid and introduced as a mist, atomised spray or by vaporisation. The method comprising: (a) maintaining the oxygen concentration at a setpoint by monitoring the oxygen concentration and following detection of the oxygen concentration has fallen below the setpoint, admitting an input containing oxygen, and permitting chamber atmosphere to exit; (b) removing oxygen from the chamber atmosphere at a rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration at the setpoint; and (c) introducing the substance into in chamber atmosphere at a predetermined rate.

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INSECTICIDE/FUNGICIDE INTRODUCED INTO CONTROLLED ATMOSPHERE CHAMBER

Field of the invention

The invention relates to the field of introducing airborne substances such as insecticides or fungicides to a chamber.

5 **Background of the invention**

In this specification, where an act or item of knowledge is referred to or discussed, this reference or discussion is not an admission that the act or item of knowledge or any combination thereof was at the priority date part of common general knowledge or known to be relevant to an attempt to solve any problem with which this specification is 10 concerned.

When transporting or storing cargo such as respiring produce or other comestibles in suitable chambers, it may be desirable to be able to apply a fungicide, an insecticide or other initially airborne substance to the cargo. However, it may be necessary to ensure that the concentration of the substance in the chamber does not substantially exceed a 15 given amount. This may be required for health reasons, legal reasons and/or to ensure the integrity of the cargo.

One method of controlling the concentration of the substance is to actively monitor the concentration of the substance in the chamber atmosphere, and to vary the rate of release of the substance into the chamber based on the concentration measurements. However, 20 depending upon the substance being introduced into the chamber, it may not be possible to design a machine that is capable of accurately measuring the concentration of the substance in question. In some applications, although it is possible to measure and actively control the concentration of the substance concerned, the machinery required to do so is expensive.

25 Accordingly, there exists a need for improved, less expensive and/or simpler means for ensuring that the concentration of a substance introduced into a chamber does not substantially exceed a given amount.

Summary of the invention

According to a first aspect of the present invention there is provided a method for 30 introducing a substance into the atmosphere within a chamber and adjusting the chamber

atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount, the method comprising:

(a) maintaining the oxygen concentration in the chamber atmosphere substantially at a predetermined oxygen setpoint by (i) monitoring the oxygen concentration in the chamber and following detection that the oxygen concentration has fallen below the setpoint, or below a predetermined margin about the setpoint (ii) admitting into the chamber an input containing oxygen in known proportion so that the amount of oxygen in the chamber increases; and (iii) causing or permitting chamber atmosphere to exit the chamber;

(b) removing oxygen from the chamber atmosphere at a rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint;

(c) independently introducing the substance into the chamber atmosphere substantially at a predetermined substance introduction rate such that the concentration of the substance in the chamber atmosphere does not substantially exceed a predetermined amount.

The input may be or include a gas mixture. It may be one or more distinct gas streams. It may be ambient air. It may be processed ambient air, such as by a splitter.

For avoidance of doubt, the reference to "continual" includes "regular" or "frequent" and is not limited to "continuous".

Preferably, the concentration of the substance in the chamber atmosphere is maintained substantially at a predetermined constant concentration in the chamber atmosphere over an operative period following an equilibrating period.

Preferably, the predetermined substance introduction rate has been calculated in accordance with a mathematical model of the proportions of chamber atmosphere constituents. A preferred mathematical model is described below.

The present invention enables a substance to be introduced into the chamber atmosphere such that the concentration of the substance is maintained substantially at a predetermined constant concentration over an operative period in a cost effective manner that does not require any active monitoring or control of the concentration of the substance in the chamber atmosphere. Rather, all that is required is oxygen control in accordance with the invention.

According to a second aspect of the present invention there is provided a method for introducing a substance into the atmosphere within a chamber containing substantially non-respiring cargo such that the concentration of the substance in the chamber atmosphere is maintained substantially at a desired constant concentration in the chamber atmosphere over an operative period following an equilibrating period, the method comprising:

(a) maintaining the oxygen concentration in the chamber atmosphere substantially at a predetermined oxygen setpoint by (i) monitoring the oxygen concentration in the chamber and following detection that the oxygen concentration has fallen below the setpoint, or below a predetermined margin about the setpoint (ii) admitting into the chamber an input containing oxygen in known proportion so that the amount of oxygen in the chamber increases; and (iii) causing or permitting chamber atmosphere to exit the chamber;

(b) removing oxygen from the chamber atmosphere substantially at a predetermined oxygen removal rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint;

(c) introducing the substance into the chamber atmosphere substantially at a predetermined substance introduction rate such that the concentration of the substance in the chamber atmosphere is maintained substantially at the desired constant concentration over the operative period.

Preferably, the concentration of the substance in the chamber atmosphere is maintained substantially at a predetermined constant concentration in the chamber atmosphere over an operative period following an equilibrating period.

Preferably, the predetermined substance introduction rate has been calculated in accordance with a mathematical model of the proportions of chamber atmosphere constituents. A preferred mathematical model is described below.

According to a third aspect of the present invention there is provided a method for adjusting the atmosphere within a chamber to enable a cargo subject to degradation by insects to be stored with reduced degradation, the method comprising:

(a) maintaining the oxygen concentration in the chamber atmosphere substantially at a predetermined oxygen setpoint by (i) monitoring the oxygen concentration in

the chamber and following detection that the oxygen concentration has fallen below the setpoint, or below a predetermined margin about the setpoint (ii) admitting into the chamber an input containing oxygen in known proportion so that the amount of oxygen in the chamber increases; and (iii) causing or permitting chamber atmosphere to exit the chamber;

(b)   removing oxygen from the chamber atmosphere at a rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint;

(c)   introducing an insecticide into the chamber atmosphere at a substantially constant predetermined insecticide introduction rate such that the insecticide concentration in the chamber atmosphere is maintained substantially at a desired insecticidally effective concentration over an operative period following an equilibrating period, the operative period being sufficient to kill at least a substantial proportion of insects in or on the cargo.

The insecticide may be carbon dioxide. Where the insecticide is carbon dioxide, the desired insecticidally effective concentration may be quite high, such as over 30% of the chamber atmosphere.

The method of the third aspect of the present invention may be applied to a chamber containing cargo which is further subject to degradation or deterioration through senescence, the method further comprising the step of, following the operative period, significantly reducing the rate of introduction of insecticide, or ceasing introduction of insecticide, and, optionally, varying the oxygen setpoint, to produce following an equilibrating period a predetermined chamber atmosphere composition, the predetermined composition being selected to delay or reduce further deterioration or further degradation of the cargo through senescence.

In this case, the atmospheric conditions for delaying further deterioration or further degradation of the cargo through senescence are preferably further selected so as to substantially limit further damage to the cargo by residual live insects.

According to a fourth aspect of the present invention, the third aspect of the invention may be applied instead to a chamber with cargo subject to degradation by fungal growth to enable the cargo to be stored with reduced degradation, the reference to "insecticidally effective concentration" being replaced by "fungicidally effective concentration" and the

reference to "killing a substantial proportion of the insects" being replaced by a reference to "killing a substantial proportion of the fungal growth".

According to a fifth aspect of the present invention there is provided a method for introducing two or more substances into the atmosphere within a chamber such that the concentrations of the substances in the chamber atmosphere are maintained substantially at respective desired constant concentrations in the chamber atmosphere over an operative period following an equilibrating period, the method comprising:

(a)   maintaining the oxygen concentration in the chamber atmosphere substantially at a predetermined oxygen setpoint by (i) monitoring the oxygen concentration in the chamber and following detection that the oxygen concentration has fallen below the setpoint, or below a predetermined margin about the setpoint (ii) admitting into the chamber an input containing oxygen in known proportion so that the amount of oxygen in the chamber increases; and (iii) causing or permitting chamber atmosphere to exit the chamber;

(b)   removing oxygen from the chamber atmosphere at a rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint;

(c)   introducing the substances into the chamber atmosphere substantially at respective predetermined substance introduction rates such that the concentrations of the substances in the chamber atmosphere are maintained substantially at the respective desired constant concentrations over the operative period.

The concentrations of the substances in the chamber atmosphere are preferably maintained substantially at respective predetermined constant concentrations in the chamber atmosphere over an operative period following an equilibrating period.

Preferably, the predetermined substance introduction rates have been calculated in accordance with a mathematical model of the proportions of chamber atmosphere constituents.

According to a further aspect of the present invention there is provided a method for introducing a substance into the atmosphere within a chamber such that the concentration of the substance within the chamber atmosphere does not substantially exceed a predetermined amount, the method comprising introducing the substance into

the chamber at one or more predetermined substantially constant rates during one or more periods of time, the predetermined rate or rates having been selected such that the concentration of the substance within the chamber atmosphere does not substantially exceed the predetermined amount. Preferably, the rate or rates are selected according to the methods described herein.

According to another aspect of the present invention there is provided a method for introducing a substance into the atmosphere within a chamber containing respiring produce and for adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount, the method comprising maintaining the oxygen concentration substantially at a predetermined oxygen setpoint according to one of the oxygen concentration control methods described herein.

Various oxygen concentration control methods are described in detail below. In summary, these methods provide for the oxygen concentration to be maintained substantially at a predetermined setpoint by admitting, or causing to be admitted, an oxygen containing gas (such as ambient atmosphere which contains approximately 21% oxygen by volume) into the chamber when the oxygen concentration falls below the setpoint (or below a point within a suitable margin or tolerance about the setpoint), and causing or permitting chamber atmosphere to exit the chamber. Typically, the amount of chamber atmosphere exiting the chamber will be approximately the same amount or volume of chamber atmosphere as admitted to the chamber.

The above methods for introducing a substance into a chamber atmosphere enable substances which should not exceed the predetermined amount, to be introduced into the chamber without any need for active monitoring of the concentration of the substance in the chamber atmosphere.

Any suitable substances may be used. The substance may be an insecticide. The substance may be a fungicide. It may be a fumigant. It may be a bactericide. The substance according to the invention may be a mixture of substances. The substance may be moisture (ie. water) to provide humidification.

In one embodiment the method may maintain humidity in a chamber containing respiring produce. In this embodiment, the method may take into account the contribution to the moisture level in the chamber atmosphere made by moisture generated by respiration. The method may take into account the contribution to the moisture level in the chamber atmosphere made by moisture in the ambient atmosphere.

Where the methods are applied to a chamber containing respiring produce, the methods may further comprise the step of removing carbon dioxide substantially at a predetermined rate, the predetermined rate having been selected such that the carbon dioxide concentration within the chamber atmosphere will not substantially exceed a predetermined amount.

According to another aspect of the present invention there is provided apparatus for introducing a substance into the atmosphere within a chamber containing respiring produce and for adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount, the apparatus comprising:

(a)   sealing means for sealing the chamber to the extent required to effect oxygen concentration control according to one of the oxygen concentration control methods described herein;

(b)   either, or both of, an openable and closeable inlet means and an openable and closeable outlet means, to permit ambient atmosphere to enter the chamber and chamber atmosphere to exit the chamber;

(c)   a controller having an oxygen concentration sensor and control means responsive to the oxygen concentration sensor, the control means being adapted to cause the inlet means and/or the outlet means, as applicable, to open to admit, or to cause to be admitted, ambient atmosphere into the chamber following the oxygen concentration sensor detecting that the oxygen concentration in the chamber has fallen below a predetermined amount; and

(d)   substance introduction means for introducing the substance into the chamber atmosphere at one or more predetermined substantially constant rates during one or more respective periods of time so that the concentration of the substance does not substantially exceed the predetermined amount.

According to a further aspect of the present invention there is provided apparatus for introducing a substance into the atmosphere within a chamber and adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount, the apparatus comprising:

(a)   a controller having an oxygen concentration sensor and control means responsive to the oxygen concentration sensor, the control means being adapted to cause to

be admitted into the chamber an input containing oxygen following the oxygen concentration sensor detecting that the oxygen concentration in the chamber has fallen below a predetermined oxygen setpoint; and

(b)   an oxygen load for removing oxygen at a rate sufficient to require continual admission of the input into the chamber to enable the action of the controller to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint; and

(c)   substance introduction means for introducing the substance into the chamber atmosphere at one or more predetermined substantially constant rates during one or more respective periods of time so that the concentration of the substance does not substantially exceed the predetermined amount.

According to a further aspect of the present invention there is provided apparatus for introducing a substance into the atmosphere within a chamber and adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount, the apparatus comprising:

(a)   substance introduction means for introducing the substance into the chamber atmosphere; and

(b)   a controller having an oxygen concentration sensor for measuring the oxygen concentration in the chamber atmosphere and control means responsive to the oxygen concentration sensor, the control means being adapted to control the substance introduction means to vary the substance introduction rate in dependence on the measured oxygen concentration in the chamber so that the concentration of the substance does not substantially exceed the predetermined amount.

These apparatus may further comprise carbon dioxide reduction means to remove carbon dioxide from the chamber atmosphere at a predetermined rate so that the carbon dioxide concentration within the chamber atmosphere will not substantially exceed a predetermined amount.

According to another aspect of the present invention, there is provided a method for converting a receptacle into an adjusted atmosphere chamber containing respiring produce, the adjusted atmosphere chamber being arranged such that a substance is

introducible into the chamber atmosphere such that the concentration of the substance will not substantially exceed a predetermined amount, the method comprising:

(a) forming a chamber in the receptacle optionally including installing sealing means to seal the chamber to the extent required to effect oxygen concentration control according to one of the methods described herein;

(b) installing one or more openings in the chamber including either, or both of, an openable and closeable inlet means and an openable and closeable outlet means, to permit ambient atmosphere to enter the chamber and chamber atmosphere to exit the chamber;

(c) installing a controller according to the present invention; and

(d) installing substance introduction means according to the present invention.

According to another aspect of the present invention, there is provided a method for converting a receptacle into an adjusted atmosphere chamber arranged such that a substance is introducible into the chamber atmosphere such that the concentration of the substance will not substantially exceed a predetermined amount, the method comprising:

(a) forming a chamber in the receptacle optionally including installing sealing means to seal the chamber to a desired extent to effect oxygen concentration control;

(b) installing a controller having an oxygen concentration sensor and control means responsive to the oxygen concentration sensor, the control means being adapted to cause to be admitted into the chamber an input containing oxygen following the oxygen concentration sensor detecting that the oxygen concentration in the chamber has fallen below a predetermined oxygen setpoint

(c) installing substance introduction means for introducing the substance into the chamber atmosphere at one or more predetermined substantially constant rates during one or more respective periods of time so that the concentration of the substance does not substantially exceed the predetermined amount.

According to a further aspect of the present invention, there is provided a method for converting a receptacle into an adjusted atmosphere chamber wherein a substance is introducible into the chamber atmosphere such that the concentration of the substance will not substantially exceed a predetermined amount, the method comprising:

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(a) forming a chamber in the receptacle optionally including installing sealing means to seal the chamber to the desired extent;

(b) installing a controller according to the present invention; and

(d) installing substance introduction means according to the present invention.

5 According to a further aspect of the present invention there is provided a receptacle when converted into an adjusted atmosphere chamber in accordance with the methods for converting a receptacle into an adjusted atmosphere chamber described herein.

Oxygen concentration control

The oxygen concentration control according to the invention may be achieved in any
10 suitable way.

Substantially sealed chamber

In a preferred arrangement for providing oxygen control, the chamber is substantially sealed (if necessary by applying appropriate sealing means to the chamber) and is provided with openable and closeable inlet and outlet means to, respectively, enable
15 oxygen containing gas (such as ambient atmosphere) to enter the chamber and chamber atmosphere to exit the chamber. The inlet and outlet means may be opened for a suitable length of time following detection that the oxygen concentration has fallen below the setpoint (or below a point within a suitable margin or tolerance about the setpoint).

Where ambient atmosphere is the oxygen containing gas, ambient atmosphere may be
20 drawn or forced into the chamber by placing the inlet means near a source of low pressure within the chamber, and/or near a source of high pressure outside the chamber. In this case, opening of the outlet means will result in chamber atmosphere being forced or drawn out from the chamber as a result of the slight increase in pressure of the chamber atmosphere following entry of the ambient atmosphere into the chamber
25 (assuming, of course, that the outlet means is not placed near a source of low pressure within the chamber, or a source of high pressure outside the chamber).

Alternatively, or additionally, chamber atmosphere may be drawn or forced out of the chamber by placing the outlet means near a source of high pressure within the chamber, and/or near a source of low pressure outside the chamber. In this case, opening of the
30 inlet means will result in chamber atmosphere being drawn into the chamber as a result of the slight decrease in pressure of the chamber atmosphere following the exit of

chamber atmosphere from the chamber (assuming, of course, that the inlet means is not placed near a source of high pressure within the chamber, or a source of low pressure outside the chamber).

5   In a preferred embodiment, the inlet means is opened for a time that is approximately proportional to the difference between the detected oxygen concentration and the oxygen setpoint.

Chamber not substantially sealed – initial pressure reduction

In another arrangement where ambient atmosphere is the oxygen containing gas, the oxygen control is effected by, following detection that the oxygen concentration in the
10   chamber has fallen below the relevant predetermined amount, causing chamber atmosphere to exit the chamber through an opening so that the pressure in the chamber is or will be reduced below ambient pressure such that ambient atmosphere is or will be drawn into the chamber through an opening so that the amount of oxygen in the chamber increases. In this arrangement, the chamber must be sealed to the extent that
15   when the pressure within the chamber is substantially equal to ambient pressure the rate of leakage of oxygen into the chamber is less than the rate of consumption of oxygen by the respiring produce, and it must be open to the extent that when the chamber pressure is less than ambient pressure as described, the rate of entry of oxygen into the chamber is greater than the rate of consumption of oxygen by the respiring produce.

20   In this arrangement, the opening to permit ambient atmosphere to enter the chamber may be the same opening as the opening to permit chamber atmosphere to exit the chamber. However, it is preferred that a distinct opening is provided in the form of an openable and closeable outlet means to permit chamber atmosphere to exit the chamber.

Chamber atmosphere may be caused to exit the chamber through an opening by locating
25   the opening near a source of high pressure inside the chamber, such that chamber atmosphere is expelled from the chamber through the opening. The source of high pressure may be supplied by a fan. In an embodiment where the chamber is formed within a refrigerated container having a refrigeration fan inside the chamber, the refrigeration fan may be used as a source of high pressure.

30   Chamber atmosphere may be caused to exit the chamber through an opening by locating the opening near a source of low pressure outside the chamber, such that chamber atmosphere is drawn out of the chamber through the opening. The source of low pressure may be supplied by a fan.

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An opening for permitting ambient atmosphere to enter the chamber may be provided wholly or partly by leakage paths into the chamber. An opening may be added to the chamber, such as by making one or more holes in the chamber. An opening may comprise existing leakage paths into the chamber.

5   In the embodiment where the opening for permitting ambient atmosphere to enter the chamber is the same as, or one of, respectively, the opening or openings for permitting chamber atmosphere to exit the chamber, ambient atmosphere may be drawn into the chamber through the opening following turning off the source of high or low pressure (as the case may be), or removing it from the vicinity of the opening, so that when the
10   pressure in the chamber is below ambient pressure, ambient atmosphere may be drawn into the chamber through the opening.

In an embodiment including outlet means, the outlet means is preferably opened for a time that is approximately proportional to the difference between the detected oxygen concentration and the oxygen setpoint.

15   *Chamber not substantially sealed – initial pressure increase*

In another arrangement where ambient atmosphere is the oxygen containing gas, the oxygen control is effected by, following detection that the oxygen concentration in the chamber has fallen below the relevant predetermined amount, causing ambient atmosphere to enter the chamber through an opening so that the amount of oxygen in
20   the chamber increases and so that the pressure in the chamber exceeds ambient pressure such that chamber atmosphere is expelled from the chamber through an opening. In this arrangement, the chamber must be sealed to the extent that when the pressure within the chamber is substantially equal to ambient pressure the rate of leakage of oxygen into the chamber is less than the rate of consumption of oxygen by the respiring produce, and it
25   must be open to the extent that when the chamber pressure is greater than ambient pressure as described, the rate of leakage of chamber atmosphere out of the chamber is sufficient to reduce the chamber pressure, before the oxygen concentration in the chamber again falls below the predetermined amount, to a level that will not prevent ambient atmosphere from entering the chamber through the opening first referred to
30   above.

In this arrangement, the opening to permit ambient atmosphere to enter the chamber may be the same opening as the opening to permit chamber atmosphere to exit the

chamber. However, it is preferred that a distinct opening is provided in the form of an openable and closeable inlet means to permit chamber atmosphere to enter the chamber.

Chamber atmosphere may be caused to enter the chamber through an opening by locating the opening near a source of low pressure inside the chamber, such that chamber atmosphere is drawn into the chamber through the opening. The source of low pressure may be supplied by a fan. In an embodiment where the chamber is formed within a refrigerated container with a refrigeration fan inside the chamber, the refrigeration fan may be used as a source of low pressure.

Chamber atmosphere may be caused to enter the chamber through an opening by locating the opening near a source of high pressure outside the chamber, such that chamber atmosphere is forced into the chamber through the opening. The source of high pressure may be supplied by a fan.

An opening for permitting chamber ambient atmosphere to exit the chamber may be provided wholly or partly by leakage paths into the chamber. An opening may be added to the chamber, such as by making one or more holes in the chamber. An opening may comprise existing leakage paths into the chamber.

In the embodiment where the opening for permitting ambient atmosphere to exit the chamber is the same as, or one of, respectively, the opening or openings for permitting chamber atmosphere to enter the chamber, ambient atmosphere may be caused to enter the chamber through the opening following turning off the source of high or low pressure (as the case may be), or removing it from the vicinity of the opening, so that when the pressure in the chamber is above ambient pressure, chamber atmosphere may be forced out of the chamber through the opening.

Following the influx of ambient atmosphere into the chamber, as stated, the pressure in the chamber will exceed ambient pressure. The pressure differential will force chamber atmosphere to exit the chamber through the opening.

In an embodiment including inlet means, the inlet means is preferably opened for a time that is approximately proportional to the difference between the detected oxygen concentration and the oxygen setpoint.

General chamber

Oxygen control can be effected in a general chamber, not necessarily substantially sealed, or partially sealed in the manner described above. The general oxygen control method used in conjunction with the present invention is as follows:

(a)   maintaining the oxygen concentration in the chamber atmosphere substantially at a predetermined oxygen setpoint by (i) monitoring the oxygen concentration in the chamber and following detection that the oxygen concentration has fallen below the setpoint, or below a predetermined margin about the setpoint (ii) admitting into the chamber an input containing oxygen in known proportion so that the amount of oxygen in the chamber increases; and (iii) causing or permitting chamber atmosphere to exit the chamber;

(b)   removing oxygen from the chamber atmosphere at a rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint;

This method may be implemented using apparatus according to the present invention.

This general method of oxygen control provides two significant advantages in connection with introducing a substance into the chamber atmosphere such that the concentration of the substance does not substantially exceed the predetermined amount.

Firstly, in the case where the cargo is intended to be respiring produce, the requirement of substantial sealing or partial sealing of the chamber as discussed above means that many containers cannot be immediately employed as modified atmosphere containers. Such containers must in many cases be rejected altogether, or be repaired to reduce the degree of leakage to a suitable level to enable the containers to be used. The inventors have realised that a chamber which is open to a greater degree than the partial sealing discussed above can be employed together with a chamber containing respiring produce by adding an oxygen load to the chamber to take up oxygen at a rate which is greater than the net rate of leakage of oxygen into the chamber less the rate of consumption of oxygen by the respiring produce at the setpoint, so that after an equilibration period, the oxygen concentration within the chamber atmosphere is maintained substantially at the setpoint.

This method enables many containers that would be too leaky to be employed in previously developed atmosphere adjustment methods to be immediately employed in the present method as a modified atmosphere container without any need for repair to reduce the degree of leakage, and without any need to have ongoing chamber atmosphere purging with a gas of low oxygen concentration.

Accordingly the method of the first embodiment of the invention may be applied to a chamber containing respiring produce, the chamber being open to the extent that the net rate of leakage of oxygen into the chamber from the ambient atmosphere is greater than the rate of consumption of oxygen by the respiring produce, wherein the oxygen containing input is provided by ambient air, and wherein the oxygen removal is effected in part by the respiring produce and in part by removing oxygen from the chamber atmosphere substantially at a predetermined oxygen removal rate, the predetermined oxygen removal rate being greater than the net rate of leakage of oxygen into the chamber less the rate of consumption of oxygen by the respiring produce at the setpoint.

The rate of consumption of oxygen by the respiring produce at the setpoint may be estimated by known methods from a knowledge of relevant data, such as the type of produce, the mass of the produce and the storage temperature. If the carbon dioxide level within the chamber atmosphere is to be adjusted as detailed below, then the maximum desired carbon dioxide level may also be taken into consideration when estimating the rate of consumption of oxygen by the respiring produce at the setpoint.

Any suitable method of estimating the net rate of leakage of oxygen into the chamber may be used, together with the estimate of the rate of consumption of oxygen by the respiring produce, as a basis for selecting the predetermined oxygen removal rate.

One method is to employ the principle that, at a constant pressure within the container, the flow rate into the container must equal the flow rate out of the container (through the various leakage paths). Accordingly, air may be pumped into the container at a known flow rate until the pressure remains constant at a particular target pressure (for example, 150 pascals above atmospheric pressure).

For a suitable target pressure such as 150 Pa above ambient pressure, the resultant flow rate represents a maximum flow rate that could occur in practice by leakage through diffusion and/or convection. In particular, under these test conditions, the pressure is substantially uniform throughout the chamber, whereas, in practice, pressure gradients will be present throughout the chamber so that a pressure difference of, say, 150 Pa, will only exist in the vicinity of a fan in the chamber.

Accordingly, an estimate of the likely maximum or upper limit of the net rate of leakage of oxygen into the chamber may be made by taking 21% of the measured leakage rate at the target pressure, since oxygen makes up approximately 21% by volume of ambient air.

Accordingly, if the predetermined oxygen removal rate is chosen to equal or exceed this maximum measure of oxygen leakage into the chamber, less the rate of oxygen consumption by the respiring produce, then the predetermined oxygen removal rate will exceed the amount required by the present invention.

5   The principle underlying this aspect of the present invention is as follows. In principle, and assuming the oxygen level in the chamber atmosphere has reached the oxygen setpoint, if oxygen were to be removed from the chamber atmosphere at a rate precisely equal to the difference between the net rate of leakage of oxygen into the chamber and the rate of consumption of oxygen by the respiring produce (being the respiration rate for 10 the produce in question at the particular oxygen setpoint), then the oxygen concentration within the chamber would remain at the setpoint. However, the invention requires oxygen to be removed from the chamber atmosphere at a greater rate. Accordingly, but for the admission of oxygen by the active oxygen monitoring and control, there would be insufficient oxygen in the chamber to meet the respiration requirement of the respiring 15 produce (at the particular oxygen setpoint). The requirement that sufficient oxygen is removed to require oxygen admission ensures that the active monitoring and control of oxygen level causes the oxygen level to be maintained substantially at the oxygen setpoint.

The second advantage of the general oxygen control method is that it allows a substance 20 to be introduced into the chamber such that it will not exceed a given concentration where respiring produce does not constitute the cargo. This has considerable advantage in enabling the method to be applied to the storage of substantially non-respiring cargo such as meat and grain which may nevertheless benefit from storage or transportation under modified atmosphere conditions to delay deterioration or degradation through 25 senescence, or where a fungicide, insecticide or other fumigant is required to prevent or reduce a particular means of deterioration or degradation of the cargo in circumstances where it is not practical to actively measure and control the fumigant concentration.

The oxygen load may be any suitable means for removing oxygen from the chamber atmosphere. Preferably, at least part of the oxygen removal is effected by contacting a 30 quantity of oxygen absorbing material with the chamber atmosphere. The oxygen absorbing material may be any suitable material for absorbing oxygen. Oxygen absorbing materials known from the field of packaging of foods may be suitable for use in the present invention. For example, one class of oxygen absorbing materials suitable for use with the invention includes finely divided iron powder which takes up oxygen in an

oxidation reaction (ie. the iron rusts). Another class of oxygen absorbing materials suitable for use with the invention contains ascorbic acid. Materials of these classes are sold under the trade name Ageless, marketed by Mitsubishi Gas Chemical Co.

5   The oxygen absorbing material is preferably contained in at least one oxygen transmissible container, such as for example an oxygen transmissible bag. Preferably, the at least one oxygen transmissible container is selected so that the rate of oxygen transmission into the at least one oxygen transmissible container is substantially equal to the predetermined oxygen removal rate.

10   Once the required oxygen reduction rate is determined, this information may be used to calculate the oxygen transmissibility properties of one or more containers of oxygen absorbing material.

Commercial films of known oxygen transmissibility are typically specified with reference to a transmission coefficient k_{O_2} which represents the flow rate of oxygen through the film (typically in litres per minute), per percent of oxygen in the atmosphere, per unit
15   area of film (typically in square metres). Thus, if the required rate of oxygen absorption is expressed in suitable flow units (designated $\dot{a}_{O_2}$) (eg units of flow rate such as litres per minute), then the product of the area of the film and the transmission coefficient will equal the quotient of the oxygen absorption rate and the oxygen equilibrium concentration. That is, $k_{O_2} A = \dfrac{\dot{a}_{O_2}}{p_{O_2}}$. Suitable oxygen transmissible containers may then
20   be selected based on the product $k_{O_2} A$.

Where the chamber cargo is non-respiring produce and it is desired to have a modified atmosphere chamber in which carbon dioxide is present in the chamber at a concentration which does not exceed a predetermined concentration, the oxygen load may include an artificial respiration load, that is an oxygen load which consumes oxygen
25   and produces carbon dioxide. Thus, the oxygen removal and carbon dioxide introduction may both be effected by an artificial respiration load.

The artificial respiration load may be provided by effecting a chemical reaction that consumes oxygen and produces carbon dioxide. The chemical reaction may produce carbon dioxide at a greater or lesser molar rate than the rate at which oxygen is

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consumed. A substance which consumes oxygen and produces carbon dioxide is a mixture of iron carbonate and ascorbic acid.

The artificial respiration load may be provided by fermentation. The artificial respiration load may be provided by combustion. It may be provided by a photosynthetic substance.
5   It may be provided by a biochemical reaction. The biochemical reaction may be an enzymatic reaction.

Timing for opening inlet/outlet means

The length of time for which the oxygen containing input is admitted (such as by opening an inlet means) and/or the length of time for which chamber atmosphere is caused or
10   permitted to exit the chamber (such as by opening an outlet means) may suitably be approximately proportional to the difference between the measured oxygen concentration and the oxygen setpoint. By "approximately proportional", we mean that the length of time the inlet means or outlet means is open should be small if the difference is small and large if the difference is large. A true proportionality in the sense
15   of a linear relationship between oxygen concentration difference and length of time of opening of the inlet means or outlet means, is not required. (This situation only arises when the measured oxygen concentration is less than the oxygen setpoint because when the measured oxygen concentration exceeds the oxygen setpoint, the inlet means and/or outlet means would remain closed.)

20   In a preferred embodiment, logic of the following form is used to control the oxygen concentration within the chamber (in this embodiment ambient air is used as the oxygen containing input):

   1.   Measurement of chamber oxygen concentration takes place at predetermined constant intervals, for example every 8 minutes.

25 2.   If the difference between the measured oxygen concentration and the oxygen setpoint is more than a predetermined margin, for example 0.9%, then an inlet means is opened to allow ambient air to enter the chamber to thereby increase the oxygen concentration within the chamber. The inlet means and/or outlet means is/are closed after the measured oxygen concentration has exceeded the oxygen
30   setpoint.

   3.   If the difference between the measured oxygen concentration and the oxygen setpoint is less than the predetermined margin, then the inlet means and/or outlet

means is/are opened to allow ambient air to enter the chamber to thereby increase the oxygen concentration within the chamber. The inlet means and/or outlet means is/are closed after a time dependent on the oxygen concentration as measured prior to opening the inlet means. Preferably the dependence on the oxygen concentration as measured takes the following form:

Setpoint - oxygen concentration (%)	Time (minutes)
range 1	time 1
range 2	time 2
range 3	time 3
etc	
lower bound of range N to the predetermined margin	time N

Initial inert gas flushing

The chamber may be flushed with a gas having a low oxygen concentration or containing no oxygen. Nitrogen may be used as the gas. Such a gas flushing step may be effected to lower the initial oxygen concentration within the chamber to below a predetermined maximum oxygen concentration. If the oxygen content is thereby lowered below a predetermined minimum oxygen concentration, the controller may operate to cause the oxygen concentration within the chamber to be increased. If such a gas flushing step were not carried out, it could take considerable time for the oxygen concentration within the chamber to be lowered as a result of the removal of oxygen, such as by the consumption of oxygen by produce during respiration.

Where the chamber contains respiring produce, the gas flushing step would typically occur after produce has been loaded into a chamber fitted with atmosphere adjustment apparatus according to the present invention.

The gas flushing step is preferably used to lower the initial oxygen concentration the chamber to within a few percent of the oxygen setpoint.

If the oxygen content is lowered to the oxygen setpoint by the action of respiring produce, in the absence of carbon dioxide control (described below) there will be an approximately proportional increase in the carbon dioxide level in the chamber.

20

Accordingly, the gas flushing step may be used to control the initial carbon dioxide concentration in the chamber atmosphere.

The gas flushing step may in theory be carried out in conjunction with any of the oxygen concentration control methods described herein. However, typically, one would only expect to go to the trouble and expense of carrying out a gas flushing step where a substantially sealed chamber is used (and where oxygen concentration control is accordingly based on the use of a substantially sealed chamber).

General chamber atmosphere constituent

The methods and apparatus of the invention may be adapted to operate based on active measurement and control of a principal chamber atmosphere constituent other than oxygen, provided that the concentration of the constituent in the chamber atmosphere can be readily measured. Thus, according to a further aspect of the invention, there is provided a method for introducing a substance into the atmosphere within a chamber and adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount, the method comprising:

(a) maintaining the concentration of a principal chamber atmosphere constituent in the chamber atmosphere substantially at a predetermined setpoint by (i) monitoring the concentration of the constituent in the chamber and following detection that the constituent concentration has fallen below the setpoint, or below a predetermined margin about the setpoint (ii) admitting into the chamber an input containing the constituent in known proportion so that the amount of the constituent in the chamber atmosphere increases; and (iii) causing or permitting chamber atmosphere to exit the chamber;

(b) removing the constituent from the chamber atmosphere at a rate sufficient to require continual admission of the input into the chamber to maintain the constituent concentration in the chamber atmosphere substantially at the setpoint;

(c) independently introducing the substance into the chamber atmosphere substantially at a predetermined substance introduction rate such that the concentration of the substance in the chamber atmosphere does not substantially exceed a predetermined amount.

As will be understood by those skilled in the art, following the example provided by the above generalisation of the scope of the invention beyond using oxygen as the relevant

constituent, the other methods and apparatus of the invention described herein may be similarly generalised, and such generalisations are envisaged to fall within the scope of the present invention.

The principal chamber atmosphere constituent subject to being maintained substantially at the setpoint could be carbon dioxide. Any suitable chamber atmosphere constituent may be used.

Introduction rate of introduced substance

Where the oxygen concentration in the chamber is substantially maintained at the setpoint in one of the ways described above, the predetermined introduction rate of the substance into the chamber atmosphere may be calculated from a formula derived from a mathematical model of the proportions of chamber atmosphere constituents. The mathematical model may be a continuous flow model. That is, notwithstanding that the flow of oxygen containing gas into the chamber, and of chamber atmosphere out of the chamber, may not be continuous flow, nevertheless, for the purpose of calculation, the flow of ambient atmosphere into the chamber, and of chamber atmosphere out of the chamber, may be modelled as being continuous flow.

It will be readily appreciated by those skilled in the art that other suitable forms of modelling the proportions of chamber atmosphere may be used, and such models are considered to fall within the scope of the present invention. A model may be based on discrete time intervals rather than using the continuous flow approximation.

The substance introduction rate is preferably calculated from a formula that produces a result substantially equal to the result produced by a calculation in accordance with the following formula:

$$R_s = a_s + p_s \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_s - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right) \qquad (1)$$

where:

R_s is the substance introduction rate;

a_s is the rate of removal of the substance from the chamber atmosphere (for avoidance of any doubt not including removal from the chamber by chamber atmosphere exiting the chamber);

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a_{O_2} is the rate of oxygen gas removal from the chamber atmosphere (for avoidance of any doubt not including removal from the chamber by chamber atmosphere exiting the chamber);

a_i is the rate of removal from the chamber atmosphere of a further constituent of the input not being oxygen gas (for avoidance of any doubt not including removal from the chamber by chamber atmosphere exiting the chamber);

X_{i,O_2} is the proportion of oxygen gas in the input divided by the proportion of the further constituent in the input;

P_{O_2} is the oxygen setpoint expressed as a proportion;

p_s is the predetermined concentration of the substance, expressed as a proportion;

Σ is the sum of the concentrations of any further principal chamber atmosphere constituents, expressed as proportions.

Equation (1) is expressed in general form and accordingly some of these quantities may be zero. For example, if the oxygen containing input includes an inert gas which is not absorbed or adsorbed from the chamber atmosphere, and is not otherwise consumed or broken down in the chamber, then a_i will be zero.

For example, where the oxygen containing gas is ambient air, then there are two constituents of the oxygen containing input gas stream, oxygen (about 21%) and nitrogen (about 79%). X_{i,O_2} is then 0.79/0.21. If the chamber contains respiring produce, then carbon dioxide will be a principal chamber atmosphere constituent and Σ will be the carbon dioxide concentration in the chamber. (The carbon dioxide concentration may be modified as discussed in relation to equation (8) below.) The introduced substance may be, for example, an insecticide which is independently introduced into the chamber atmosphere. In these circumstances, a_i in equation (1) will represent the rate of removal from the chamber atmosphere of nitrogen, which will be zero because nitrogen is not removed from the chamber atmosphere at all. Accordingly, in these circumstances equation (1) will reduce to:

$$R_s = a_s + \frac{0.79 r_{O_2} \cdot p_s}{0.21 - 0.21 p_s - 0.21 p_{CO_2} - p_{O_2}} \qquad (2)$$

where:

r_{O_2} is the respiration rate of produce in the chamber; and

p_{CO_2} is the equilibrium carbon dioxide concentration.

For many introduced substances, a suitable model of the rate of removal of the substance
from the chamber atmosphere will be absorption or adsorption of the substance from the
chamber atmosphere at a rate proportional to the concentration of the substance in the
chamber atmosphere. For example, the substance may be absorbed or adsorbed into or
onto the chamber walls and/or objects within the chamber, such as the cargo.

That is, where appropriate, a_s may be modelled by a formula that produces a result
substantially equal to the result produced by a calculation in accordance with the
following formula:

$$a_s = k_s \cdot p_s \tag{3}$$

The constant of proportionality k_s may be calculated as follows:

$$k_s = \sum_i k_i A_i \tag{4}$$

where k_i and A_i represent, respectively, constants of proportionality and areas of
different surface types of the boundary and of objects within the chamber.

In the method of the fifth aspect of the present invention, the substance introduction rate
may be calculated from a formula that produces a result substantially equal to the result
produced by a calculation in accordance with the following formulae:

where:

$$R_{s_1} = a_{s_1} + p_{s_1} \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_{s_1} - p_{s_2} - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right)$$

$$R_{s_2} = a_{s_2} + p_{s_2} \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_{s_1} - p_{s_2} - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right)$$

R_{s_1} and R_{s_2} are the substance introduction rates;

a_{s_1} and a_{s_2} are the rates of removal of the substances from the chamber atmosphere;

a_{O_2} is the rate of oxygen gas removal from the chamber atmosphere;

a_i is the rate of removal from the chamber atmosphere of a further constituent of the gas stream not being oxygen gas;

5   X_{i,O_2} is the proportion of the further constituent in the gas stream divided by the proportion of oxygen gas in the gas stream;

P_{O_2} is the oxygen setpoint expressed as a proportion;

Σ is the sum of the concentrations of any further principal chamber atmosphere constituents, expressed as proportions.

10   <u>Substance introduction means</u>

Any suitable form of substance introduction means may be used. In one embodiment, the substance introduction means comprises a storage for the substance and one or more associated atomisers for introducing the substance into the chamber atmosphere as a fine mist or spray. The introduced substance may be a liquid. It may be a gas. The substance
15   may be provided by being dissolved in a suitable solvent. The substance may be, or be dissolved in, a volatile liquid, and be introduced by vaporisation.

<u>Further control of chamber atmosphere</u>

The method of the first aspect of the present invention, in which the substance is independently introduced into the chamber atmosphere, may be applied to a chamber
20   containing respiring produce. In this case carbon dioxide will be a principal chamber atmosphere constituent. In this case, the method may further comprise removing carbon dioxide from the chamber atmosphere substantially at a predetermined carbon dioxide removal rate, the predetermined carbon dioxide removal rate having been selected such that the carbon dioxide concentration within the chamber atmosphere does not
25   substantially exceed a predetermined amount lower than the carbon dioxide concentration which would result if no carbon dioxide removal was effected.

In this case, the predetermined substance introduction rate and the predetermined carbon dioxide removal rate may be calculated in accordance with a mathematical model of the proportions of chamber atmosphere constituents. Preferably, the substance

introduction rate and the carbon dioxide removal rate are calculated from formulae that produce results substantially equal to the results produced by calculations in accordance with the following formulae:

$$R_s = a_s + p_s \cdot \left(\frac{X_{i,o_2} a_{o_2} - a_i}{1 - p_s - p_{CO_2} - \Sigma - \left(1 + X_{i,o_2} \right) p_{o_2}} \right) \qquad (5)$$

$$a_{CO_2} = R_{CO_2} - p_{CO_2} \cdot \left(\frac{X_{i,o_2} a_{o_2} - a_i}{1 - p_s - p_{CO_2} - \Sigma - \left(1 + X_{i,o_2} \right) p_{o_2}} \right) \qquad (6)$$

where:

R_s is the substance introduction rate;

a_s is the rate of removal of the substance from the chamber atmosphere;

a_{o_2} is the rate of oxygen gas removal from the chamber atmosphere;

a_i is the rate of removal from the chamber atmosphere of a further constituent of the input not being oxygen gas;

X_{i,o_2} is the proportion of the further constituent in the input divided by the proportion of oxygen gas in the input;

p_{o_2} is the oxygen setpoint expressed as a proportion;

p_s is the predetermined concentration of the substance, expressed as a proportion;

a_{CO_2} is the rate of carbon dioxide removal from the chamber atmosphere;

p_{CO_2} is the carbon dioxide concentration in the chamber atmosphere expressed as a proportion; and

Σ is the sum of the concentrations of any further principal chamber atmosphere constituents, expressed as proportions.

If no carbon dioxide removal is to be effected, then the resultant equilibrium carbon dioxide concentration may be estimated from equation (6) by setting $a_{CO_2} = 0$ and solving for p_{CO_2}.

For the case where the method of the first aspect of the invention is applied to a chamber containing respiring produce and where the oxygen containing gas is ambient atmosphere, then if the carbon dioxide concentration within the chamber is not being controlled or adjusted, the equilibrium carbon dioxide concentration may be calculated from a formula that produces a result substantially equal to the result produced by a calculation in accordance with the following formula:

$$p_{CO_2} = RQ \cdot \frac{0.21 - p_{O_2} - 0.21 p_s}{0.79 + 0.21 RQ} \qquad (7)$$

where RQ is the respiration quotient of respiring produce in the chamber. ($RQ = \frac{r_{CO_2}}{r_{O_2}}$ where r_{O_2} is the rate of oxygen consumption through respiration and r_{CO_2} is the rate of production of carbon dioxide through respiration (whether normalised or in suitable units).)

The equilibrium carbon dioxide concentration may be allowed to result simply from the maintenance of the oxygen concentration within the chamber substantially at the setpoint without any steps being taken to control the carbon dioxide concentration. However, if it is desired to modify the equilibrium carbon dioxide concentration which would result if no modification were undertaken, then the carbon dioxide concentration may be adjusted by active carbon dioxide adjustment or passive carbon dioxide adjustment.

If it is desired to modify the equilibrium carbon dioxide concentration which would result if no modification were undertaken, then the carbon dioxide concentration may be passively adjusted by removing carbon dioxide from the chamber substantially at a predetermined rate. The predetermined carbon dioxide removal rate is preferably calculated from a formula that produces a result substantially equal to the result produced by a calculation in accordance with the following formula:

$$a_{CO_2} = r_{CO_2} - \frac{0.79 r_{O_2} \cdot p_{CO_2}}{0.21 - 0.21 p_s - 0.21 p_{CO_2} - p_{O_2}} \qquad (8)$$

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where r_{CO_2} is the rate of production of carbon dioxide through respiration, a_{CO_2} is the carbon dioxide removal rate and p_{CO_2} represents the desired carbon dioxide equilibrium concentration.

Once the required carbon dioxide absorption rate a_{CO_2} is known, this information may be used to calculate the carbon dioxide transmissibility properties of one or more containers of carbon dioxide absorbing material, such as bags of lime.

Commercial films of known carbon dioxide transmissibility are typically specified with reference to a transmission coefficient k_{CO_2} which represents the flow rate of carbon dioxide through the film (typically in litres per minute), per percent of carbon dioxide in the atmosphere, per unit area of film (typically in square metres). Thus, if the required rate of carbon dioxide absorption is expressed in suitable flow units (designated a'_{CO_2}) (eg units of flow rate such as litres per minute), then the product of the area of the film and the transmission coefficient will equal the quotient of the carbon dioxide absorption rate and the carbon dioxide equilibrium concentration. That is, $k_{CO_2} A = \dfrac{a'_{CO_2}}{p_{CO_2, eq}}$. Suitable carbon dioxide transmissible containers may then be selected based on the product $k_{CO_2} A$.

According to the method of the present invention, the predicted equilibrium carbon dioxide concentration in the chamber can be set in advance so that it will reach the desired level by using a carbon dioxide concentration reduction means (such as carbon dioxide transmissible containers filled with carbon dioxide absorbing material).

The amount of carbon dioxide absorbing material placed in the carbon dioxide transmissible containers should be sufficient to be capable of absorbing all the carbon dioxide that enters the carbon dioxide transmissible containers and therefore needs to be a sufficient amount to last the estimated time of storage of produce within the chamber.

In the method of the second aspect of the invention, the substance may be introduced independently of the oxygen removal.

In the method of the second aspect of the invention, in which a substance is introduced into a chamber containing substantially non-respiring cargo, as described above it may be desired to have a modified atmosphere chamber in which carbon dioxide is present in the

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chamber at a concentration which does not substantially exceed a predetermined concentration. In this circumstance, carbon dioxide may be the introduced substance. Further in this circumstance, oxygen removal and carbon dioxide introduction may be effected by an artificial respiration load, that is an oxygen load which consumes oxygen

5   and produces carbon dioxide. Possible artificial respiration loads have been discussed above.

Where the second aspect of the invention is applied to a chamber in which the introduced substance is carbon dioxide and where oxygen removal and carbon dioxide introduction are effected by an artificial respiration load, it may be desirable to modify the carbon

10   dioxide concentration from that which would result simply from the maintenance of the oxygen concentration substantially at the setpoint without any steps being taken to control the carbon dioxide concentration, so that the carbon dioxide concentration within the chamber atmosphere does not substantially exceed a predetermined amount. In this case, carbon dioxide will be a principal chamber atmosphere constituent and the method

15   may further comprise removing carbon dioxide from the chamber atmosphere substantially at a predetermined carbon dioxide removal rate, the predetermined carbon dioxide removal rate having been selected such that the carbon dioxide concentration within the chamber atmosphere does not substantially exceed a predetermined amount lower than the carbon dioxide concentration which would result if no carbon dioxide

20   removal was effected.

In this case, the predetermined carbon dioxide introduction rate and the predetermined carbon dioxide removal rate may be calculated in accordance with a mathematical model of the proportions of chamber atmosphere constituents. Preferably, the carbon dioxide removal rate is calculated from a formula that produces a result substantially equal to the

25   result produced by a calculation in accordance with the following formula:

$$a_{CO_2} = R_{CO_2} - p_{CO_2} \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_{CO_2} - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right) \qquad (9)$$

where:

a_{CO_2} is the rate of carbon dioxide removal from the chamber atmosphere;

R_{CO_2} is the carbon dioxide introduction rate;

30   a_{O_2} is the rate of oxygen gas removal from the chamber atmosphere;

a_i is the rate of removal from the chamber atmosphere of a further constituent of the input not being oxygen gas;

X_{i,O_2} is the proportion of the further constituent in the input divided by the proportion of oxygen gas in the input;

5 P_{O_2} is the oxygen setpoint expressed as a proportion;

P_{CO_2} is the carbon dioxide concentration in the chamber atmosphere expressed as a proportion; and

Σ is the sum of the concentrations of any further principal chamber atmosphere constituents, expressed as proportions.

10 Further control of introduced substance concentration

When the chamber of the present invention is to have an adjusted atmosphere where the oxygen concentration is maintained substantially at a predetermined concentration (the oxygen setpoint), in the absence of an inert gas purging operation, the oxygen level must first degrade from the atmospheric proportion (around 21%) to the setpoint.

15 If the oxygen concentration control is based on having a substantially sealed chamber, then during the time the oxygen level degrades from the atmospheric proportion to the setpoint, the chamber will be substantially sealed. When the chamber is substantially sealed, release of the introduced substance at the rate determined in accordance with equation (1) may result in the concentration of the substance overshooting the desired

20 equilibrium level of the substance. Once the oxygen setpoint is reached so that the oxygen containing gas is being continually admitted to the chamber to replenish consumed oxygen and chamber atmosphere is being continually expelled from the chamber, the concentration of the introduced substance will return substantially to the equilibrium level predicted in accordance with equation (1).

25 In some applications, overshoot, if it occurs, is of no concern since the concentration of introduced substance will return substantially to its equilibrium level. However, there may be other applications, such as the introduction of fungicides, insecticides or other fumigants, in which it is desirable that overshoot be avoided. Accordingly, the methods of the present invention may comprise the step of introducing the substance at a rate prior

30 to the oxygen concentration attaining the setpoint which is different from the rate of introduction of the substance following the oxygen concentration attaining the setpoint.

When the chamber is substantially sealed, based on a model in which the respiration rate r_{O_2} of produce in the chamber is constant, the time $t_{\to O_2, eq}$ taken for the oxygen setpoint to be attained is given by:

$$t_{\to O_2, eq} = \frac{I_{O_2} - p_{O_2, eq}}{r_{O_2}} \qquad (10)$$

5   where I_{O_2} is the initial normalised oxygen concentration in the chamber, $p_{O_2, eq}$ is the oxygen setpoint and r_{O_2} is the normalised rate of oxygen consumption through respiration (the normalisation being with respect to chamber volume).

When the chamber is substantially sealed, the variation of the concentration of the introduced substance is as follows:

10
$$p_f(t) = \frac{R_f}{k_f} - \left(\frac{R_f}{k_f} - I_f \right) e^{-k_f t} \qquad (11)$$

If, using equation (11), $p_f \left(t_{\to O_2, eq} \right) > p_{f, eq}$ then overshoot will occur. By inspection from equation (11), assuming that the initial concentration of the introduced substance I_f is less than the desired equilibrium concentration $p_{f, eq}$ of the introduced substance, the concentration $p_f(t)$ of the introduced substance will approach, but not substantially

15   exceed, $\frac{R_f}{k_f}$. Consequently, if under these circumstances the release rate R_f is set to

$k_f \cdot p_{f, eq}$ then overshoot will not occur ($p_{f, eq}$ here represents the level of the introduced substance that it is desired be maintained after the oxygen setpoint is reached, but not overshot beforehand). Conveniently, the release rate R_f may simply be set to $k_f \cdot p_{f, eq}$ prior to the oxygen setpoint being reached irrespective of whether overshoot would

20   otherwise be expected to have occurred in order to ensure that overshoot will not occur.

According to an aspect of the present invention there is provided a method for introducing a substance into the atmosphere within a chamber such that the concentration of the substance within the chamber atmosphere does not substantially exceed a predetermined amount, wherein the substance is introduced at one or more first

25   release rates prior to the oxygen concentration attaining the oxygen setpoint and wherein

the substance is introduced at one or more second release rates subsequent to the oxygen concentration attaining the oxygen setpoint.

If the oxygen concentration control is based on one of the methods described above in which the chamber is not substantially sealed, then during the time the oxygen level degrades from the atmospheric proportion (or other initial proportion) to the setpoint, the chamber will be expected to have some leakage (since it is not substantially sealed). However, the average flow rate out of the chamber will not be as high as when the oxygen setpoint is reached since the method of oxygen control will not be actively admitting ambient atmosphere and expelling chamber atmosphere until the setpoint is reached. Accordingly, during the time the oxygen concentration is degraded by the oxygen removal from its initial value to the setpoint, release of the introduced substance at the rate determined in accordance with equation (1) may result in the concentration of the substance overshooting the desired equilibrium level of the substance.

In these circumstances, if it is desired to avoid the concentration of the introduced substance overshooting the desired equilibrium level of the substance, the rate of introduction of the substance will need to be reduced in comparison to that which is calculated for the case when the oxygen setpoint is reached (ie. the release rate determined in accordance with equation (1)). According to one method of calculating or estimating an appropriate release rate for this circumstance, the maximum concentration of the substance in the chamber is first determined for the case where there is some leakage from the chamber.

Conveniently, this circumstance is similar to that where a substance is introduced into a chamber that is not substantially sealed and that contains respiring produce, where no adjustment of the chamber atmosphere takes place. (In some circumstances it will be desirable to introduce a substance into a chamber that is not substantially sealed that contains respiring produce such that the concentration of the substance does not substantially exceed a predetermined amount, but without otherwise adjusting the chamber atmosphere.)

Under these conditions, and based on a continuous flow model, the concentration of the substance will be expected to reach (but will not substantially exceed) the following level:

$$p_{f,eq} = \frac{R_f}{k_f + f_{v_2}}$$ (12)

where f_{v_2} is the normalised outflow rate of chamber atmosphere.

Where atmosphere adjustment is being effected in a chamber that is not substantially sealed, outflow may result from leakage from the chamber. Where atmosphere adjustment is not being effected, outflow may also result from leakage from the chamber. Where atmosphere adjustment is not being effected, outflow may result from forced ventilation. The nature of the outflow is not important.

The substance may be introduced at a rate such that the concentration of the substance does not substantially exceed a predetermined amount if the outflow rate of chamber atmosphere f_{v_2} can be measured or pre-estimated (the other quantities in equation (12) being known or controllable). Because the oxygen concentration in the chamber is relatively easy to measure, a convenient method for determining the chamber outflow rate may be based on the measurement of oxygen concentration and the knowledge, or an estimate, of the rate of removal of oxygen from the chamber, such as by respiration of produce or provision of an oxygen load.

It is assumed here that the outflow rate is substantially constant for at least substantial periods of time. Where the outflow rate remains substantially constant within a given period, the outflow for that period may be used in calculations or estimates, and the outflow rates for other periods used for calculating or estimating outflow rates for such other periods.

Using a continuous flow model that assumes the chamber inflow rate and the chamber outflow rate are constant and equal, the outflow rate f_{v_2} can be calculated from the following expression, which depends only on the respiration rate and measured oxygen concentrations:

$$f_{v_2} = \frac{p'_{O_2}(t) + r_{O_2}}{0.21 - p_{O_2}(t)} \qquad (13)$$

In one embodiment of the present invention, $p_{O_2}(t)$ is modeled as a straight line for the purposes of applying equation (13) so that its derivative $p'_{O_2}(t)$ may be easily determined. Provided the time scale is sufficiently short, this approximation will not be unreasonable.

The appropriate release rate may then be calculated from equation (12):

33

$$R_f = p_{f,eq} \cdot \left(k_f + f_{v_2}\right) \qquad\qquad (14)$$

(ie. the release rate to ensure that the predetermined maximum concentration of introduced substance is not substantially exceeded (a) during the period in which the oxygen concentration degrades to the setpoint, or (b) where there is no atmosphere adjustment, at any time during the storage of produce).

According to another aspect of the present invention, there is provided a method for introducing a substance into the atmosphere within a chamber such that the concentration of the substance within the chamber atmosphere does not substantially exceed a predetermined amount, selection of the rate being calculated in dependence on a pre-estimate or a measurement of the outflow rate of chamber atmosphere from the chamber.

Preferably, the outflow rate of chamber atmosphere from the chamber is calculated in dependence on measured concentrations of a different atmospheric constituent within the chamber atmosphere. Preferably, the different atmospheric constituent within the chamber atmosphere is oxygen.

It may be desirable to be able to arrange for the concentration of the introduced substance within the chamber atmosphere to be substantially zero at a particular time, such as by the end of the intended transit and/or storage time of items, such as produce, stored within the chamber. In the various arrangements according to the present invention described herein, if the substance ceases to be introduced into the chamber, the concentration of the substance within the chamber atmosphere will decrease. Using a continuous flow model, the concentration of the substance will vary as follows after the substance introduction means is switched off or otherwise deactivated:

$$p_f(t) = I_f e^{-(k_f + f_{v_2})t} \qquad\qquad (15)$$

where the initial concentration I_f is the concentration of the substance at the moment the substance introduction means is deactivated. If it is assumed that the substance concentration was approximately equal to the desired or estimated equilibrium concentration $p_{f,eq}$ when the substance introduction means is deactivated (ie. $I_f = p_{f,eq}$), one can determine how long prior to the intended time the substance introduction means must be deactivated.

It is convenient to define a time constant τ as follows:

$$\tau = \frac{1}{k_f + f_{v_2}} \qquad (16)$$

which will be in units of time (typically, minutes or hours).

The substance concentration within the chamber will decrease from the initial
concentration I_f to the following levels after time has elapsed following deactivation of
the substance introduction means:

Elapsed time	Predicted substance concentration
τ	$0.37 I_f$
2τ	$0.14 I_f$
3τ	$0.05 I_f$
$n\tau$	$I_f e^{-n}$

Thus, for example, if in a particular application a final concentration of the order of 0.05
times the equilibrium substance concentration is acceptable, then the substance
introduction means may be deactivated at a time of 3τ hours prior to the relevant time.

Controller

A controller according to the present invention includes sensor means and control means.
Where oxygen concentration control is used, or when the controller must otherwise
measure oxygen concentrations, the sensor means is operable for sensing the
concentration of oxygen. The sensor means may also sense other variables within the
chamber, for example, humidity. Preferably the sensor means includes an oxygen
concentration measurement device which provides an output in the form of an electrical
signal containing information about the oxygen concentration level within the chamber.
Such an electrical signal may be a direct current signal having voltage proportional to
oxygen concentration or the signal may digitally encode the oxygen concentration level or
a number that is proportional, or otherwise in known relation to, the oxygen
concentration. Other forms of output are also envisaged within the scope of the present
invention.

A controller according to the present invention comprises means to receive and respond to the sensor means output. Such response may include activating devices subject to the control of the controller. The response may include activating one or more valves. It may include signalling the substance introduction means to commence introducing the

5   substance, to halt introducing the substance, or to vary the substance introduction rate.

The controller may be operatively connected to the devices under its control by direct wire connection or any other suitable means.

The controller may receive signals from the sensor means continuously. It may sample the signals discontinuously. Where the signals are sampled discontinuously, the sampling

10 intervals may be equal or unequal. The sampling interval may be made to vary according to the output of the sensor means or may be fixed.

Where the controller is required to measure or estimate a chamber outflow rate, or other quantity not directly measured, based on a method requiring numerous direct measurements of the concentration of a chamber atmosphere constituent (typically

15 oxygen) (for example, equation (13)), the controller includes measurement memory for retrievably storing a series of measurements from the sensor means.

Where the controller program is required to perform calculations in dependence on measured data (for example, a controller program implementing the method described with reference to equation (13)), the controller must include sufficient computing power

20 to effect the calculations.

Not all hardware or software components of the controller need to be physically part of the controller. Some components may be located adjacent the controller and in communication with the controller. They may be remote from the controller with suitable communication means employed to enable the control means and/or the sensor

25 means to communicate with the components. Suitable communication means may include telecommunications, mobile telephony, Internet connections, satellite transmissions, or any other suitable means for remotely communicating data, including any combination of the foregoing.

Sealing means

30 Sealing means according to the present invention is provided to seal the chamber to the required extent. In some forms of the present invention, notably those forms utilising inlet means and outlet means, the chamber is preferably substantially sealed. Where inlet

means and/or outlet means are used in conjunction with an opening in the chamber and the chamber must be sealed to the extent that, when the pressure within the chamber is substantially equal to ambient pressure the rate of leakage of oxygen into the chamber is less than the rate of consumption of oxygen by the respiring produce, sealing means may

5   be used or not, as necessary.

Preferably a chamber according to the present invention containing respiring produce is sealed to a sufficient extent that the rate of consumption of oxygen by the respiring produce within the chamber exceeds the rate of leakage of oxygen into the chamber.

It has been found useful to conduct tests on receptacles intended to be converted into

10   chambers of the present invention to determine the leakage rate in order to determine whether they may be immediately employed in accordance with the present invention or whether they should be rejected or repaired. The presently preferred testing method for use in relation to receptacles in the form of (empty) shipping containers is to first seal a container with sealing means according to the present invention (to be discussed below).

15   Following sealing, air is pumped into the container at a regulated flow rate through an appropriate fitting in an air vent in the container. At another air vent, there is provided a manometer tapping to measure the pressure inside the container.

The preferred testing method employs the principle that, at a constant pressure within the container, the flow rate into the container must equal the flow rate out of the

20   container (through the various leakage paths). Accordingly, the flow rate of air being pumped into the container is adjusted until the pressure remains constant at a particular target pressure, preferably 150 pascals above atmospheric pressure.

In the case of a 20 foot long standard refrigerated shipping container, at that pressure, a container with a leakage rate of no more than about 10 to 12 litres per minute typically

25   represents a container suitable for conversion to a substantially sealed chamber in accordance with the present invention, without any need for repair. In the case of a 40 foot long standard refrigerated shipping container, at the stated pressure, a container with a leakage rate of no more than about 20 to 25 litres per minute typically represents a container suitable for conversion to a substantially sealed chamber in accordance with the

30   present invention without any need for repair. It will be appreciated by those skilled in the art that the appropriate degree of air tightness for a container depends upon whether the produce to be stored has a high or low respiration rate and that the figures quoted are only a guide.

The sealing means acts as a barrier to the passage of gas into or out of the chamber. The sealing means may act as a moisture barrier. The chamber may comprise substantially the entire internal volume of the receptacle or a reduced volume within the chamber.

5   The point of entry to a chamber is liable to leak. The point of entry to a chamber is typically in the form of one or more doors. In particular, it has been found that for shipping containers, the seals of the doors of the container are generally the source of most leakage. Consequently, the sealing means provided in accordance with the present invention may include door sealing means.

10   The sealing means provided by the present invention may also include a curtain. The curtain may comprise a substantially fluid impervious sheet. The curtain may substantially seal an open end of a receptacle to form the chamber. The curtain may seal the chamber from leakage paths in the receptacle that are outside the chamber. In particular, the curtain may seal the chamber from any leakage paths in the door seals of the receptacle by being interposed between the chamber and receptacle door.

15   A curtain may be attached to the internal and/or external walls of the receptacle by any suitable means. Adhesive, including tape or glue, may be used.

      In a preferred embodiment of the present invention, there is provided a curtain for use in conjunction with a receptacle made from a magnetic material, such as a steel shipping container. The curtain is provided with numerous permanent magnets adjacent its
20   periphery for attaching the curtain to the receptacle. In a particularly preferred embodiment for use in conjunction with a steel shipping container, the curtain is installed in the container when the doors are open by attaching the magnets to the external walls of the container. Once the curtain is suitably placed, the doors of the container are closed to thereby substantially seal the curtain against the container.

25   A curtain according to one aspect of the present invention is preferably located close to the door of the receptacle in order to maximise the volume of the chamber. The curtain is preferably approximately coplanar with the receptacle door when the curtain is in a substantially un-deformed state where there is equal pressure on either side of the curtain.

30   Refrigerated shipping containers (sometimes known as reefer containers) are generally of a standard style of construction. Such containers typically have a false floor. The stored items, such as produce, sits on the false floor which is spaced from the outer wall of the container to facilitate air flow within the container. The false floor typically terminates a

short distance from the end of the container to facilitate air flow at the ends of the load stored within the container.

The curtain is preferably located within the space between the container door and the beginning of the false floor.

5 In this arrangement the chamber is accordingly bounded by the container walls and the curtain with the space between the curtain and the container door being outside the chamber.

The sealing means provided in accordance with the present invention may also include a cover for any ventilation port in the shipping container or other receptacle. The cover

10 may comprise a sheet of flexible material such as an expanded rubber sheet. The sheet may be initially oversized and subsequently trimmed on site to form a cover which matches the profile of the ventilation port whereby to seal it. The cover may be installed over the ventilation port by any means. Preferably the cover is adhered to the port and/or the wall immediately surrounding the port with tape and/or glue. Where a port comprises

15 a number of apertures, one or more covers may be used to seal the port.

The cover is substantially impermeable. The cover may include one or more layers which are not substantially impermeable. In this case, the cover may include a substantially impermeable layer such as an adhesive sheet to adhere the cover to the port and/or the wall immediately surrounding the port. The substantially impermeable adhesive sheet is

20 preferably applied so as to substantially cover the permeable material. In this way the cover may be rendered substantially impermeable.

Inlet means and outlet means

25 Openable and closeable inlet and outlet means provided in accordance with the present invention are operable to facilitate respectively the inflow of ambient atmosphere into the chamber and the outflow of chamber atmosphere from the chamber.

Inlet and outlet means each comprise one or more valves operable to provide in an open position communication between the chamber atmosphere within the chamber and the

30 ambient atmosphere surrounding the chamber.

Inlet means and outlet means may be located in any boundary of the chamber.

In a typical arrangement, the outlet means is located adjacent to a fan provided in the chamber for circulating air within the chamber. Preferably, the outlet means is mounted in a ventilation port near the fan. In the case of a standard refrigerated shipping container having a fan at one end of the container, the outlet means is preferably

5   mounted in the ventilation port that is typically located adjacent to the fan.

The outlet means is preferably located on the high pressure side of the fan so that when the outlet is open, chamber atmosphere is forced out of the chamber.

Where both inlet means and outlet means are used, the inlet means is preferably spaced from the outlet means. Preferably the arrangement of the inlet means and outlet means is

10   such as to facilitate the free flow of atmosphere between the interior and exterior of the chamber. Most preferably the inlet and outlet means are positioned relative to one another so as to facilitate cross-flow ventilation when each is in the open position.

Preferably the inlet and outlet means are located at either end of the chamber. The inlet means or outlet means may be mounted in a curtain according to the present invention.

15   In this case, installation of the curtain also includes installation of the inlet means or outlet means. The inlet means and the outlet means may each include a plurality of valves. Such valves may be spaced from one another in locations which facilitate the desired air flow.

The valves comprising the inlet and outlet means may be operable in response to a signal

20   from the controller. Each valve may communicate with the controller by wire or any other suitable means.

Each valve provided according to the present invention may be magnetically operable between an open position and a closed position. A solenoid is preferably provided to generate a magnetic field in response to the application of a direct current whereby to

25   urge the valve toward an open or a closed position dependent upon current direction.

Valves suitable for comprising inlet and outlet means according to the present invention are preferably electromagnetically actuable valves having a solenoid so that they may be opened from a closed position and closed from an open position by applying direct electric current to the solenoid, said one or more valves being held in either the open

30   position or the closed position in the absence of the application of said direct electric current.

Valves according to the present invention preferably may be both opened from a closed position and closed from an open position by applying a pulse of direct electric current to the solenoid. Preferably, the valves are adapted to be held in the closed position or the open position in the absence of an electric current in the solenoid by magnetic forces.

5   According to an aspect of the present invention, a valve comprising the inlet or outlet means comprises a bore, a member moveable within the bore, at least one sealing surface associated with the member, at least one aperture through which fluid may pass to pass through the valve, a solenoid adapted to generate a magnetic field in the bore in response to the application of a direct electric current, the member being adapted to move with

10   respect to the bore in response to said magnetic field between a valve open position wherein fluid passes through said at least one aperture and a valve closed position wherein said at least one sealing surface prevents fluid passing through each said at least one aperture. Preferably, the member is a slidable within the bore. Preferably, the slidable member carries at least one cover adapted to cover each said at least one aperture

15   to prevent fluid passing through said at least one aperture.

According to an aspect of the present invention, a valve comprising the inlet or outlet means comprises at least one aperture through which fluid may pass to pass through the valve, a solenoid to generate a magnetic field in response to the application of a direct electric current and a flap which is adapted to move in response to said magnetic field

20   between a valve open position wherein fluid may pass through the valve through said at least one aperture and a valve closed position wherein the flap prevents fluid passing through the valve through any said at least one aperture.

Preferably, the solenoid is located between the flap and a member carried by the flap, the member and the flap each having a permanent magnet so arranged that when a direct

25   electric current is passed through the valve in one direction the solenoid attracts the magnet on the member and repulses the magnet on the flap in order to move the flap to a valve open position and when a direct electric current is passed through the solenoid in a direction opposite to said one direction the solenoid repulses the magnet on the member and attracts the magnet on the flap in order to move the flap to a valve closed position.

30   Preferably an armature is provided in the solenoid and the flap may held in the valve open position in the absence of an electric current in the solenoid by the magnetic attraction between the armature and the magnet on the member, and the flap may held in the valve closed position in the absence of an electric current in the solenoid by the magnetic attraction between the armature and the magnet on the flap.

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In one preferred form a valve comprises a magnetic member moveable along a bore in response to the field generated by passing a direct current through a solenoid surrounding the bore. The member may be captured within the bore and moveable between positions which open and close the valve.

5   The magnetic member may take any suitable shape. The magnetic member may be a ball. It may be a right circular cylinder. It may be a prismatic member having a cross-section of any suitable shape. Other magnetic member shapes are envisaged within the scope of the invention.

In one embodiment of this principle, the magnetic member is in the form of a ball. The
10 valve contains a hole through which fluid must pass to pass through the valve. The ball seals the valve by sealingly abutting the edge of the hole. Preferably the hole is a hole in a plate in the valve. The diameter of the ball is greater than the diameter of the hole.

In another embodiment of this principle, the magnetic member is in the form of a member which is slidable with respect to the valve body. Preferably, the slidable member
15 is a cylindrical rod. The slidable member carries a cover with a sealing surface. Preferably the cover is a panel with an annular sealing surface. The fluid path through the valve when the valve is open includes one or more holes. Preferably the holes are holes in a plate in the valve. The cover seals the valve by sealingly abutting the surface around the holes. Where the cover is a panel with an annular sealing surface, the valve is closed by
20 the annular sealing surface sealingly abutting the surface around the holes. The outer diameter of the annular sealing surface is greater than the diameter of a circle surrounding the hole or holes. Preferably, the inner diameter of the annular sealing surface is also greater than the diameter of a circle surrounding the hole or holes.

In another preferred form the valve comprises a flap moveable under the application of a
25 magnetic field between open and closed positions. The flap may carry a magnet. The flap may be hingedly mounted with respect to a base. The base may carry a solenoid or coil for generating a magnetic field to open or close the flap and hence the valve in response to a signal from the controller.

A valve according to the present invention may be provided with a casing. Any such
30 casing must allow sufficient fluid flow through the valve when the valve is open. The casing may only partially encase the valve. The casing may be apertured. In particular, a casing may contain holes. Such holes may be any suitable shape. They may be circular.

They may be slots. Other aperture shapes are envisaged within the scope of the invention.

Where a valve according to the present invention has an apertured casing, preferably the apertures are located so that any relative movement between the valve and the contents of

5 the chamber or another part of the chamber will not prevent fluid flowing through the valve when the valve is open. In particular, where a valve with an apertured casing is mounted on a curtain according to the present invention, preferably the apertures are located so that the apertures will not be obstructed so as to ensure that the flow of fluid is not restricted to any significant extent.

10 For example, where a valve with a casing is mounted in a curtain which is approximately coplanar with the receptacle door when the curtain is in a substantially un-deformed state, preferably the casing includes apertures on the side of the valve rather than, or in addition to, the front or back face of the valve so that if the valve moves so that the front or back face abuts the door or another object with its front or back face, the apertures will

15 not thereby be obstructed.

Where there is a curtain according to the present invention that is flexible, the differential between the pressures of the atmospheres on each side of the curtain may vary at different points on the curtain. This variation can cause the curtain to move somewhat erratically. To facilitate equalisation of the pressure differential over the surface of the

20 curtain, the curtain may be provided with inlet means or outlet means in the form of valves, or openings, that are spaced apart. In a typical arrangement a curtain may carry inlet means or outlet means in the form of a pair of valves. One valve may be located in the upper portion and the other in the lower portion of the curtain.

As can be appreciated by those skilled in the art, the above described preferred locations

25 of the outlet means and the inlet means may be interchanged whereby the outlet means may be located in a curtain according to the present invention and the inlet means may be located near the fan. In this configuration the inlet means communicates with one of the apertures of the ventilation port that is located near the fan provided in the chamber for circulating air within the chamber. Such an inlet means is to be located on the low

30 pressure side of the fan so that when the inlet means is open, the atmosphere outside the chamber is pushed into the chamber. In this arrangement outlet means may be mounted in a curtain according to the present invention.

Description of the drawing

An embodiment of the invention will now be described with reference to the accompanying drawing in which figure 1 is a schematic side view of a standard refrigerated container fitted with atmosphere adjustment apparatus according to an embodiment of the present invention.

Figure 1 shows a receptacle in the form of refrigerated container 10 which includes refrigeration unit 12, doors 14 and ventilation port 18.

Container 10 has been converted into an adjusted atmosphere chamber 11. The atmosphere adjustment apparatus installed in container 10 are to adjust the chamber atmosphere so that is has a desired oxygen concentration and a desired carbon dioxide concentration and so that a fungicide may be applied to the chamber in such a manner that its concentration will not substantially exceed a predetermined level, subject to the additional constraint that the fungicide concentration in chamber 11 is to be substantially zero when container 10 reaches its destination.

Sealing means is provided in the form of a curtain 16 and a cover (not shown) for ventilation port 18.

Curtain 16 is an impervious sheet, and is attached to the external walls of container 10 with numerous permanent magnets mounted on the curtain adjacent its periphery. Curtain 16 is installed in the container when the doors are open by attaching the magnets to the external walls of the container. Once the curtain is suitably placed, the doors are closed to thereby substantially seal the curtain against the container. Installation of the curtain in the container defines a chamber 11 within the container.

The cover for ventilation port 18 located at the machinery end of container 10 comprises an impervious plastic sheet adhered with tape to the wall of container 10. The cover is adapted to cover, and hence seal, ventilation port 18. The cover is fitted with outlet means in the form of a valve 20.

Valve 20 is located on the high pressure side of the fan so that when valve 20 is open, the chamber atmosphere is forced out of the chamber.

Inlet means in the form of valves 100 are located in the curtain 16. Ambient atmosphere may enter chamber 11 when valves 100 are open.

44

Controller 8 includes sensor means (not shown) in the form of an oxygen concentration measurement device. The sensor means takes oxygen concentration measurements at equally spaced intervals (which may be adjusted).

5   In the present embodiment, the cargo is to comprise respiring produce. Prior to closing the chamber, the desired oxygen setpoint, desired equilibrium carbon dioxide concentration and desired fungicide concentration are determined based on the particular type of produce forming the cargo.

Carbon dioxide reduction means 9 comprising a quantity of hydrated lime held in carbon dioxide transmissible bags is located within chamber 11. The quantity of lime, the size

10   and number of lime bags and the carbon dioxide transmissibility of the bags are determined as described above (ie. as described with reference to equation (8)) based on the desired oxygen setpoint, desired equilibrium carbon dioxide concentration, desired fungicide concentration and predicted produce respiration rate.

Oxygen concentration control is effected as follows. If the oxygen concentration falls

15   below a predetermined value (for example, 5%) then controller 8 sends a signal via wires 17 to open valves 100 and 20. This allows the inflow of ambient atmosphere into chamber 11 through valves 100 and the outflow of chamber atmosphere from chamber 11 through valve 20.

Valves 20 and 100 are controlled by the controller according to the following logic:

20   1.   Measurement of chamber oxygen concentration takes place every 8 minutes.

2.   If the difference between the measured oxygen concentration and the oxygen setpoint is more than 0.9%, then controller 8 opens valves 20 and 100 to allow ambient air to enter the chamber to thereby increase the oxygen concentration within the chamber. (For the avoidance of doubt, the reference to "0.9%" is in

25   units of chamber oxygen concentration and does not represent a proportion of the oxygen setpoint.) Valves 20 and 100 are closed after controller 9 senses that the oxygen concentration has exceeded the oxygen setpoint.

3.   If the measured oxygen concentration is in the range 0 to 0.9% less than the oxygen setpoint, then controller 8 opens valves 20 and 100 to allow ambient air to

30   enter the chamber to thereby increase the oxygen concentration within the chamber. Controller 8 closes valves 20 and 100 after a time that is dependent on

45

the oxygen concentration as measured by the controller 8 prior to opening the valves, as follows:

Setpoint - oxygen concentration (%)	Time (minutes)
above 0 to 0.09	1.5
above 0.09 to 0.18	2
above 0.18 to 0.27	2.5
above 0.27 to 0.36	3
above 0.36 to 0.45	3.5
above 0.45 to 0.54	4
above 0.54 to 0.63	4.5
above 0.63 to 0.72	5
above 0.72 to 0.81	5.5
above 0.81 to 0.9	6

Valves 20 and 100 are both electromagnetically actuable valves and thus each include a solenoid. These valves are arranged so that the application of direct electric current in one direction opens the valves and the application of direct electric current in the opposite direction closes the valves. The valves are arranged to be held by permanent magnets in either the open position or the closed position in the absence of the application of the direct electric current, in order to reduce the power requirements of the controller.

When the chamber 11 is initially established and the controller program commences execution, the oxygen concentration within the chamber will be the same as the concentration of oxygen in ambient air (ie. approximately 21%). The valves 20 and 100 will accordingly remain shut at least until the oxygen concentration within the chamber reaches the setpoint.

Fungicide is introduced into the atmosphere of chamber 11 by means of atomiser 30. Atomiser 30 is connected to controller 8 by wires 31.

In order to ensure that the fungicide does not overshoot its predetermined maximum concentration, the controller is programmed to cause atomiser 30 to release fungicide at a first predetermined constant release rate R_f of $k_f \cdot p_{f,eq}$ (as described above with reference to equation (11)) prior to controller 8 sensing that the oxygen setpoint has been reached.

Controller 8 is programmed to change the fungicide release rate R_f to a second predetermined constant release rate once controller 8 senses that the oxygen setpoint has been reached, the rate being determined in accordance with equation (2) above.

Controller 8 is programmed to switch off atomiser 30 at a time of 3τ prior to the expected destination time, where τ is determined in accordance with equation (16), so that the fungicide concentration will be substantially zero at the required time.

The word 'comprising' and forms of the word 'comprising' as used in this description does not limit the invention claimed to exclude any variants or additions.

Modifications and improvements to the invention will be readily apparent to those skilled in the art. Such modifications and improvements are intended to be within the scope of this invention.

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Appendix

This appendix contains further information relating to some of the equations used herein.

<u>Variation of fungicide concentration</u>

In general:

5
$$p_f(t) = I_f + \int_0^t R_f(t')dt' - \int_0^t a_f(t')dt' - \int_0^t f_{v_2}(t')p_f(t')dt' \qquad (1.1)$$

where:

- I_f is the normalised initial fungicide concentration (ie. $p_f(0)$);

- $\int_0^t R_f(t')dt'$ is the normalised accumulation within the chamber of fungicide released at normalised release rate $R_f(t)$;

10 - $\int_0^t a_f(t')dt'$ is the normalised quantity of fungicide adsorbed on the surfaces within the chamber at normalised adsorption rate $a_f(t)$; and

- $\int_0^t f_{v_2}(t')p_f(t')dt'$ is the normalised quantity of fungicide expelled through the outlet of the chamber based on a normalised outflow rate of $f_{v_2}(t)$.

All normalisations are with respect to chamber volume, so that the terms of equation (1.1)
15 are all expressed as dimensionless proportions.

Differentiating (1.1) with respect to t:

$$p_f'(t) = R_f(t) - a_f(t) - f_{v_2}(t) \cdot p_f(t) \qquad (1.2)$$

One model for the absorption/adsorption rate $a_f(t)$ is given by:

$$a_f(t) = k_f \cdot p_f(t) \qquad (1.3)$$

20 where k_f is a constant of proportionality.

If $R_f(t)$ and $f_{v_2}(t)$ are constant, and using the model of equation (1.3), equation (1.2) may be simplified as follows:

48

$$p_f'(t) + \left(k_f + f_{v_2} \right) p_f(t) = R_f \qquad (1.4)$$

The solution to differential equation (1.4) is given by:

$$p_f(t) = \frac{R_f}{k_f + f_{v_2}} - \left(\frac{R_f}{k_f + f_{v_2}} - I_f \right) e^{-(k_f + f_{v_2})t} \qquad (1.5)$$

Equation (1.5) thus tends towards an equilibrium level of:

5

$$p_{f.eq} = \frac{R_f}{k_f + f_{v_2}} \qquad (1.6)$$

Variation of oxygen concentration

Using the same approach as that used to derive equation (1.2), the differential equation defining the variation of oxygen concentration in the chamber is:

$$p_{O_2}'(t) = 0.21 f_{v_1} - r_{O_2} - f_{v_2} \cdot p_{O_2}(t) \qquad (2.1)$$

10   where r_{O_2} is the normalised respiration rate of produce in the chamber.

Employing a model whereby $f_{v_1}(t)$ and $f_{v_2}(t)$ are constant and non-zero, the solution of equation (2.1) is:

$$p_{O_2}(t) = \frac{0.21 f_{v_1} - r_{O_2}}{f_{v_2}} - \left(\frac{0.21 f_{v_1} - r_{O_2}}{f_{v_2}} - I_{O_2} \right) e^{-f_{v_2} t} \qquad (2.2)$$

Thus, the oxygen concentration tends towards an equilibrium level of:

15

$$p_{O_2.eq} = \frac{0.21 f_{v_1} - r_{O_2}}{f_{v_2}} \qquad (2.3)$$

If $f_{v_1}(t)$ and $f_{v_2}(t)$ are both zero (ie. the chamber is sealed), then equation (2.1) becomes:

$$p_{O_2}'(t) = -r_{O_2} \qquad (2.4)$$

with the solution:

20

$$p_{O_2}(t) = I_{O_2} - r_{O_2} \cdot t \qquad (2.5)$$

49

Variation of nitrogen concentration

Similarly, employing a model whereby $f_{v_1}(t)$ and $f_{v_2}(t)$ are constant, it can be shown that:

$$p_{N_2}(t) = \frac{0.79 f_{v_1}}{f_{v_2}} - \left(\frac{0.79 f_{v_1}}{f_{v_2}} - I_{N_2} \right) e^{-f_{v_2} t} \qquad (3.1)$$

5   Thus the nitrogen concentration tends towards an equilibrium level of:

$$p_{N_2,eq} = \frac{0.79 f_{v_1}}{f_{v_2}} \qquad (3.2)$$

Variation of carbon dioxide concentration

By analogy with equation (1.3), one model for carbon dioxide absorption by a passive carbon dioxide absorbing means is as follows:

10    $$a_{CO_2}(t) = k_{CO_2} \cdot p_{CO_2}(t) \qquad (4.1)$$

Again, using a model whereby $f_{v_1}(t)$ and $f_{v_2}(t)$ are constant, it can be shown that:

$$p_{CO_2}(t) = \frac{r_{CO_2}}{k_{CO_2} + f_{v_2}} - \left(\frac{r_{CO_2}}{k_{CO_2} + f_{v_2}} - I_{CO_2} \right) e^{-(k_{CO_2} + f_{v_2}) t} \qquad (4.2)$$

Thus the carbon dioxide concentration tends towards an equilibrium level of:

$$p_{CO_2,eq} = \frac{r_{CO_2}}{k_{CO_2} + f_{v_2}} \qquad (4.3)$$

15   ## Equilibrium model

Equations (1.6), (2.3), (3.2) and (4.3) give rise to a simple model for the case when all atmospheric constituents are at equilibrium. Manipulation of these expressions yields the following expressions, respectively, for fungicide release rate and carbon dioxide absorption rate:

20    $$R_f = k_f \cdot p_{f,eq} + \frac{0.79 r_{O_2} \cdot p_{f,eq}}{0.21 - p_{O_2,eq} - 0.21 p_{CO_2,eq} - 0.21 p_{f,eq}} \qquad (5.1)$$

$$a_{CO_2} = r_{CO_2} - \frac{0.79 r_{O_2} \cdot p_{CO_2,eq}}{0.21 - p_{O_2,eq} - 0.21 p_{CO_2,eq} - 0.21 p_{f,eq}}$$ (5.2)

Modified atmosphere chamber

One model for a modified atmosphere chamber based on active oxygen level control is to consider the chamber to be sealed until the oxygen concentration has attained the setpoint ($p_{O_2,eq}$), so that $f_{v_1} = f_{v_2} = 0$, and then once the setpoint is attained to consider f_{v_1} and f_{v_2} to be constants.

Using equation (2.5), the time to attain the oxygen setpoint $t_{\rightarrow O_2,eq}$ is given by:

$$t_{\rightarrow O_2,eq} = \frac{I_{O_2} - p_{O_2,eq}}{r_{O_2}}$$ (6.1)

When $f_{v_1} = f_{v_2} = 0$, using equation (1.5), fungicide concentration varies as follows:

$$p_f(t) = \frac{R_f}{k_f} - \left(\frac{R_f}{k_f} - I_f\right) e^{-k_f t}$$ (6.2)

Thus, if $p_f\left(t_{\rightarrow O_2,eq}\right) > p_{f,eq}$, then the fungicide concentration will overshoot the desired fungicide concentration.

Assuming that the initial fungicide concentration is less than the desired fungicide concentration, from equation (6.2) the fungicide concentration $p_f(t)$ will approach $\frac{R_f}{k_f}$ from below. Accordingly, one method of avoiding overshoot is to set the fungicide release rate during the period when the chamber is sealed to the following:

$$R_f = k_f \cdot p_{f,max}$$ (6.3)

Once the oxygen setpoint has been released, the fungicide release rate can be changed to the value given by equation (5.1).

Chamber not adjusted atmosphere or not substantially sealed

If the chamber contains respiring produce and is ventilated or otherwise not substantially sealed, then the fungicide concentration in the chamber may be estimated based on an

estimate of the outflow rate from the chamber f_{v_2}. One model is to consider that the inflow rate is equal to the outflow rate, ie. $f_{v_1} = f_{v_2}$. From equation (2.1), f_{v_2} is then given by:

$$f_{v_2} = \frac{p'_{O_2} + r_{O_2}}{0.21 - p_{O_2}} \tag{7.1}$$

5   Hence f_{v_2} may be estimated from knowledge of r_{O_2} and measurement of p_{O_2} (and calculation of p'_{O_2} from p_{O_2}). In particular if $p_{O_2}(t)$ is modelled as a straight line (which will be a reasonable approximation over sufficiently short time scales) then f_{v_2} may be easily estimated from the measurement of oxygen concentrations.

Using equation (1.6), the appropriate fungicide release rate can be calculated based on
10 the desired fungicide concentration, as follows:

$$R_f = p_f \cdot (k_f + f) \tag{7.2}$$

The word 'comprising' or forms of the word 'comprising' as used in this description and in the claims do not limit the invention claimed to exclude any variants or additions.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for introducing a substance into the atmosphere within a chamber and adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount, the method comprising:

   (a) maintaining the oxygen concentration in the chamber atmosphere substantially at a predetermined oxygen setpoint by (i) monitoring the oxygen concentration in the chamber and following detection that the oxygen concentration has fallen below the setpoint, or below a predetermined margin about the setpoint (ii) admitting into the chamber an input containing oxygen in known proportion so that the amount of oxygen in the chamber increases; and (iii) causing or permitting chamber atmosphere to exit the chamber;

   (b) removing oxygen from the chamber atmosphere at a rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint;

   (c) independently introducing the substance into the chamber atmosphere substantially at a predetermined substance introduction rate such that the concentration of the substance in the chamber atmosphere does not substantially exceed a predetermined amount.

2. A method according to claim 1 wherein the concentration of the substance in the chamber atmosphere is maintained substantially at a predetermined constant concentration in the chamber atmosphere over an operative period following an equilibrating period.

3. A method according to claim 1 or claim 2 wherein the predetermined substance introduction rate has been calculated in accordance with a mathematical model of the proportions of chamber atmosphere constituents.

4. A method according to claim 3 wherein the substance introduction rate is calculated from a formula that produces a result substantially equal to the result produced by a calculation in accordance with the following formula:

$$R_s = a_s + p_s \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_s - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right)$$

where:

R_s is the substance introduction rate;

a_s is the rate of removal of the substance from the chamber atmosphere;

5   a_{O_2} is the rate of oxygen gas removal from the chamber atmosphere;

a_i is the rate of removal from the chamber atmosphere of a further constituent of the input not being oxygen gas;

X_{i,O_2} is the proportion of the further constituent in the input divided by the proportion of oxygen gas in the input;

10   p_{O_2} is the oxygen setpoint expressed as a proportion;

p_s is the predetermined concentration of the substance, expressed as a proportion;

Σ is the sum of the concentrations of any further principal chamber atmosphere constituents, expressed as proportions.

15 5. A method according to any one of claims 1 to 4 applied to a chamber containing respiring produce, the method further comprising removing carbon dioxide from the chamber atmosphere substantially at a predetermined carbon dioxide removal rate, the predetermined carbon dioxide removal rate having been selected such that the carbon dioxide concentration within the chamber atmosphere does not
20   substantially exceed a predetermined amount lower than the carbon dioxide concentration which would result if no carbon dioxide removal was effected.

6. A method according to claim 5 wherein the predetermined substance introduction rate and the predetermined carbon dioxide removal rate have been calculated in accordance with a mathematical model of the proportions of chamber atmosphere
25   constituents.

7.   A method according to claim 6 wherein the substance introduction rate and the carbon dioxide removal rate are calculated from formulae that produce results substantially equal to the results produced by calculations in accordance with the following formulae:

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$$R_s = a_s + p_s \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_s - p_{CO_2} - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right)$$

$$a_{CO_2} = R_{CO_2} - p_{CO_2} \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_s - p_{CO_2} - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right)$$

where:

R_s is the substance introduction rate;

R_{CO_2} is the rate of introduction of carbon dioxide by the respiring produce;

10   a_s is the rate of removal of the substance from the chamber atmosphere;

a_{O_2} is the rate of oxygen gas removal from the chamber atmosphere;

a_i is the rate of removal from the chamber atmosphere of a further constituent of the input not being oxygen gas;

X_{i,O_2} is the proportion of the further constituent in the input divided by the

15   proportion of oxygen gas in the input;

p_{O_2} is the oxygen setpoint expressed as a proportion;

p_s is the predetermined concentration of the substance, expressed as a proportion;

a_{CO_2} is the rate of carbon dioxide removal from the chamber atmosphere;

20   p_{CO_2} is the carbon dioxide concentration in the chamber atmosphere expressed as a proportion; and

Σ is the sum of the concentrations of any further principal chamber atmosphere constituents, expressed as proportions.

8. A method according to any one of claims 1 to 7 applied to a chamber containing respiring produce, the chamber being open to the extent that the net rate of leakage of oxygen into the chamber from the ambient atmosphere is greater than the rate of consumption of oxygen by the respiring produce, wherein the oxygen containing input is provided by ambient air, and wherein the oxygen removal is effected in part by the respiring produce and in part by removing oxygen from the chamber atmosphere substantially at a predetermined oxygen removal rate, the predetermined oxygen removal rate being greater than the net rate of leakage of oxygen into the chamber less the rate of consumption of oxygen by the respiring produce at the setpoint.

9. A method according to any one of claims 1 to 8 wherein the substance is introduced at a rate prior to the oxygen concentration attaining the setpoint which is different from the rate of introduction of the substance following the oxygen concentration attaining the setpoint.

10. A method for introducing a substance into the atmosphere within a chamber containing substantially non-respiring cargo such that the concentration of the substance in the chamber atmosphere is maintained substantially at a desired constant concentration in the chamber atmosphere over an operative period following an equilibrating period, the method comprising:

    (a) maintaining the oxygen concentration in the chamber atmosphere substantially at a predetermined oxygen setpoint by (i) monitoring the oxygen concentration in the chamber and following detection that the oxygen concentration has fallen below the setpoint, or below a predetermined margin about the setpoint (ii) admitting into the chamber an input containing oxygen in known proportion so that the amount of oxygen in the chamber increases; and (iii) causing or permitting chamber atmosphere to exit the chamber;

    (b) removing oxygen from the chamber atmosphere substantially at a predetermined oxygen removal rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint;

    (c) introducing the substance into the chamber atmosphere substantially at a predetermined substance introduction rate such that the concentration of

the substance in the chamber atmosphere is maintained substantially at the desired constant concentration over the operative period.

11. A method according to claim 10 wherein the concentration of the substance in the chamber atmosphere is maintained substantially at a predetermined constant concentration in the chamber atmosphere over an operative period following an equilibrating period.

12. A method according to claim 10 or claim 11 wherein the predetermined substance introduction rate has been calculated in accordance with a mathematical model of the proportions of chamber atmosphere constituents.

13. A method according to claim 12 wherein the substance introduction rate is calculated from a formula that produces a result substantially equal to the result produced by a calculation in accordance with the following formula:

$$R_s = a_s + p_s \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_s - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right)$$

where:

R_s is the substance introduction rate;

a_s is the rate of removal of the substance from the chamber atmosphere;

a_{O_2} is the rate of oxygen gas removal from the chamber atmosphere;

a_i is the rate of removal from the chamber atmosphere of a further constituent of the input not being oxygen gas;

X_{i,O_2} is the proportion of the further constituent in the input divided by the proportion of oxygen gas in the input;

p_{O_2} is the oxygen setpoint expressed as a proportion;

p_s is the predetermined concentration of the substance, expressed as a proportion;

Σ is the sum of the concentrations of any further principal chamber atmosphere constituents, expressed as proportions.

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14.   A method according to any one of claims 10 to 13 wherein the substance introduced into the chamber atmosphere is carbon dioxide, and wherein oxygen removal and carbon dioxide introduction are effected by an artificial respiration load.

5   15.   A method according to claim 14 wherein the artificial respiration load is provided by effecting a chemical reaction that consumes oxygen and produces carbon dioxide.

16.   A method according to claim 15 wherein the chemical reaction produces carbon dioxide at a greater or lesser molar rate than the rate at which oxygen is
10   consumed.

17.   A method according to claim 14 wherein the artificial respiration load is provided by fermentation.

18.   A method according to claim 14 wherein the artificial respiration load is provided by combustion.

15   19.   A method according to claim 14 wherein the artificial respiration load is provided by a photosynthetic substance.

20.   A method according to claim 14 wherein the artificial respiration load is provided by a biochemical reaction.

21.   A method according to claim 20 wherein the biochemical reaction is provided by
20   an enzymatic reaction.

22.   A method according to any one of claims 14 to 21 further comprising removing carbon dioxide from the chamber atmosphere substantially at a predetermined carbon dioxide removal rate, the predetermined carbon dioxide removal rate having been selected such that the carbon dioxide concentration within the
25   chamber atmosphere does not substantially exceed a predetermined amount lower than the carbon dioxide concentration which would result if no carbon dioxide removal was effected.

23.   A method according to claim 22 wherein the predetermined carbon dioxide introduction rate and the predetermined carbon dioxide removal rate have been
30   calculated in accordance with a mathematical model of the proportions of chamber atmosphere constituents.

24. A method according to claim 23 wherein the carbon dioxide removal rate is calculated from a formula that produces a result substantially equal to the result produced by a calculation in accordance with the following formula:

$$a_{CO_2} = R_{CO_2} - p_{CO_2} \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_s - p_{CO_2} - \Sigma - (1 + X_{i,O_2}) p_{O_2}} \right)$$

5   where:

R_{CO_2} is the carbon dioxide introduction rate.

a_{O_2} is the rate of oxygen gas removal from the chamber atmosphere;

a_i is the rate of removal from the chamber atmosphere of a further constituent of the input not being oxygen gas;

10   X_{i,O_2} is the proportion of the further constituent in the input divided by the proportion of oxygen gas in the input;

p_{O_2} is the oxygen setpoint expressed as a proportion;

a_{CO_2} is the rate of carbon dioxide removal from the chamber atmosphere;

p_{CO_2} is the carbon dioxide concentration in the chamber atmosphere expressed as
15   a proportion; and

Σ is the sum of the concentrations of any further principal chamber atmosphere constituents, expressed as proportions.

25. A method according to any one of claims 10 to 13 wherein the substance is introduced independently of the oxygen removal.

20   26. A method according to any one of claims 10 to 25 wherein the substance is introduced at a rate prior to the oxygen concentration attaining the setpoint which is different from the rate of introduction of the substance following the oxygen concentration attaining the setpoint.

27. A method for adjusting the atmosphere within a chamber to enable a cargo subject
25   to degradation by insects to be stored with reduced degradation, the method comprising:

(a)   maintaining the oxygen concentration in the chamber atmosphere substantially at a predetermined oxygen setpoint by (i) monitoring the oxygen concentration in the chamber and following detection that the oxygen concentration has fallen below the setpoint, or below a predetermined margin about the setpoint (ii) admitting into the chamber an input containing oxygen in known proportion so that the amount of oxygen in the chamber increases; and (iii) causing or permitting chamber atmosphere to exit the chamber;

(b)   removing oxygen from the chamber atmosphere at a rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint;

(c)   introducing an insecticide into the chamber atmosphere at a substantially constant predetermined insecticide introduction rate such that the insecticide concentration in the chamber atmosphere is maintained substantially at a desired insecticidally effective concentration over an operative period following an equilibrating period, the operative period being sufficient to kill at least a substantial proportion of insects in or on the cargo.

28.   A method according to claim 27 wherein the insecticide is carbon dioxide.

29.   A method according to claim 27 or claim 28 applied to a chamber containing cargo which is further subject to degradation or deterioration through senescence, the method further comprising the step of, following the operative period, significantly reducing the rate of introduction of insecticide, or ceasing introduction of insecticide, and, optionally, varying the oxygen setpoint, to produce following an equilibrating period a predetermined chamber atmosphere composition, the predetermined composition being selected to delay or reduce further deterioration or further degradation of the cargo through senescence.

30.   A method according to claim 29 wherein the atmospheric conditions for delaying further deterioration or further degradation of the cargo through senescence are further selected so as to substantially limit further damage to the cargo by residual live insects.

31.   A method for introducing two or more substances into the atmosphere within a
       chamber such that the concentrations of the substances in the chamber
       atmosphere do not substantially exceed respective predetermined amounts:

       (a)   maintaining the oxygen concentration in the chamber atmosphere
              substantially at a predetermined oxygen setpoint by (i) monitoring the
              oxygen concentration in the chamber and following detection that the
              oxygen concentration has fallen below the setpoint, or below a
              predetermined margin about the setpoint (ii) admitting into the chamber
              an input containing oxygen in known proportion so that the amount of
              oxygen in the chamber increases; and (iii) causing or permitting chamber
              atmosphere to exit the chamber;

       (b)   removing oxygen from the chamber atmosphere at a rate sufficient to
              require continual admission of the input into the chamber to maintain the
              oxygen concentration in the chamber atmosphere substantially at the
              setpoint;

       (c)   introducing the substances into the chamber atmosphere substantially at
              respective predetermined substance introduction rates such that the
              concentrations of the substances do not substantially exceed respective
              predetermined amounts.

32.   A method according to claim 31 wherein the concentrations of the substances in
       the chamber atmosphere are maintained substantially at respective predetermined
       constant concentrations in the chamber atmosphere over an operative period
       following an equilibrating period.

33.   A method according to claim 31 or claim 32 wherein the predetermined substance
       introduction rates have been calculated in accordance with a mathematical model
       of the proportions of chamber atmosphere constituents.

34.   A method according to claim 33 wherein the substance introduction rate is
       calculated from a formula that produces a result substantially equal to the result
       produced by a calculation in accordance with the following formulae:

       where:

$$R_{s_1} = a_{s_1} + p_{s_1} \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_{s_1} - p_{s_2} - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right)$$

$$R_{s_2} = a_{s_2} + p_{s_2} \cdot \left(\frac{X_{i,O_2} a_{O_2} - a_i}{1 - p_{s_1} - p_{s_2} - \Sigma - \left(1 + X_{i,O_2}\right) p_{O_2}} \right)$$

R_{s_1} and R_{s_2} are the substance introduction rates;

a_{s_1} and a_{s_2} are the rates of removal of the substances from the chamber atmosphere;

a_{O_2} is the rate of oxygen gas removal from the chamber atmosphere;

a_i is the rate of removal from the chamber atmosphere of a further constituent of the input not being oxygen gas;

X_{i,O_2} is the proportion of the further constituent in the input divided by the proportion of oxygen gas in the input;

p_{O_2} is the oxygen setpoint expressed as a proportion;

Σ is the sum of the concentrations of any further principal chamber atmosphere constituents, expressed as proportions.

35. Apparatus for introducing a substance into the atmosphere within a chamber and adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount, the apparatus comprising:

(a) a controller having an oxygen concentration sensor and control means responsive to the oxygen concentration sensor, the control means being adapted to cause to be admitted into the chamber an input containing oxygen following the oxygen concentration sensor detecting that the oxygen concentration in the chamber has fallen below a predetermined oxygen setpoint; and

(b) an oxygen load for removing oxygen at a rate sufficient to require continual admission of the input into the chamber to enable the action of the

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controller to maintain the oxygen concentration in the chamber atmosphere substantially at the setpoint; and

(c)   substance introduction means for introducing the substance into the chamber atmosphere at one or more predetermined substantially constant rates during one or more respective periods of time so that the concentration of the substance does not substantially exceed the predetermined amount.

36.   Apparatus for introducing a substance into the atmosphere within a chamber and adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount, the apparatus comprising:

(a)   substance introduction means for introducing the substance into the chamber atmosphere; and

(b)   a controller having an oxygen concentration sensor for measuring the oxygen concentration in the chamber atmosphere and control means responsive to the oxygen concentration sensor, the control means being adapted to control the substance introduction means to vary the substance introduction rate in dependence on the measured oxygen concentration in the chamber so that the concentration of the substance does not substantially exceed the predetermined amount.

37.   Apparatus according to claim 35 or claim 36 further comprising carbon dioxide reduction means to remove carbon dioxide from the chamber atmosphere at a predetermined rate so that the carbon dioxide concentration within the chamber atmosphere will not substantially exceed a predetermined amount.

38.   A method for converting a receptacle into an adjusted atmosphere chamber arranged such that a substance is introducible into the chamber atmosphere such that the concentration of the substance will not substantially exceed a predetermined amount, the method comprising:

(a)   forming a chamber in the receptacle optionally including installing sealing means to seal the chamber to a desired extent to effect oxygen concentration control;

(b)   installing a controller having an oxygen concentration sensor and control means responsive to the oxygen concentration sensor, the control means

being adapted to cause to be admitted into the chamber an input containing oxygen following the oxygen concentration sensor detecting that the oxygen concentration in the chamber has fallen below a predetermined oxygen setpoint

5   (c)   installing substance introduction means for introducing the substance into the chamber atmosphere at one or more predetermined substantially constant rates during one or more respective periods of time so that the concentration of the substance does not substantially exceed the predetermined amount.

10   39.   A receptacle when converted into an adjusted atmosphere chamber in accordance with the method of claim 38.
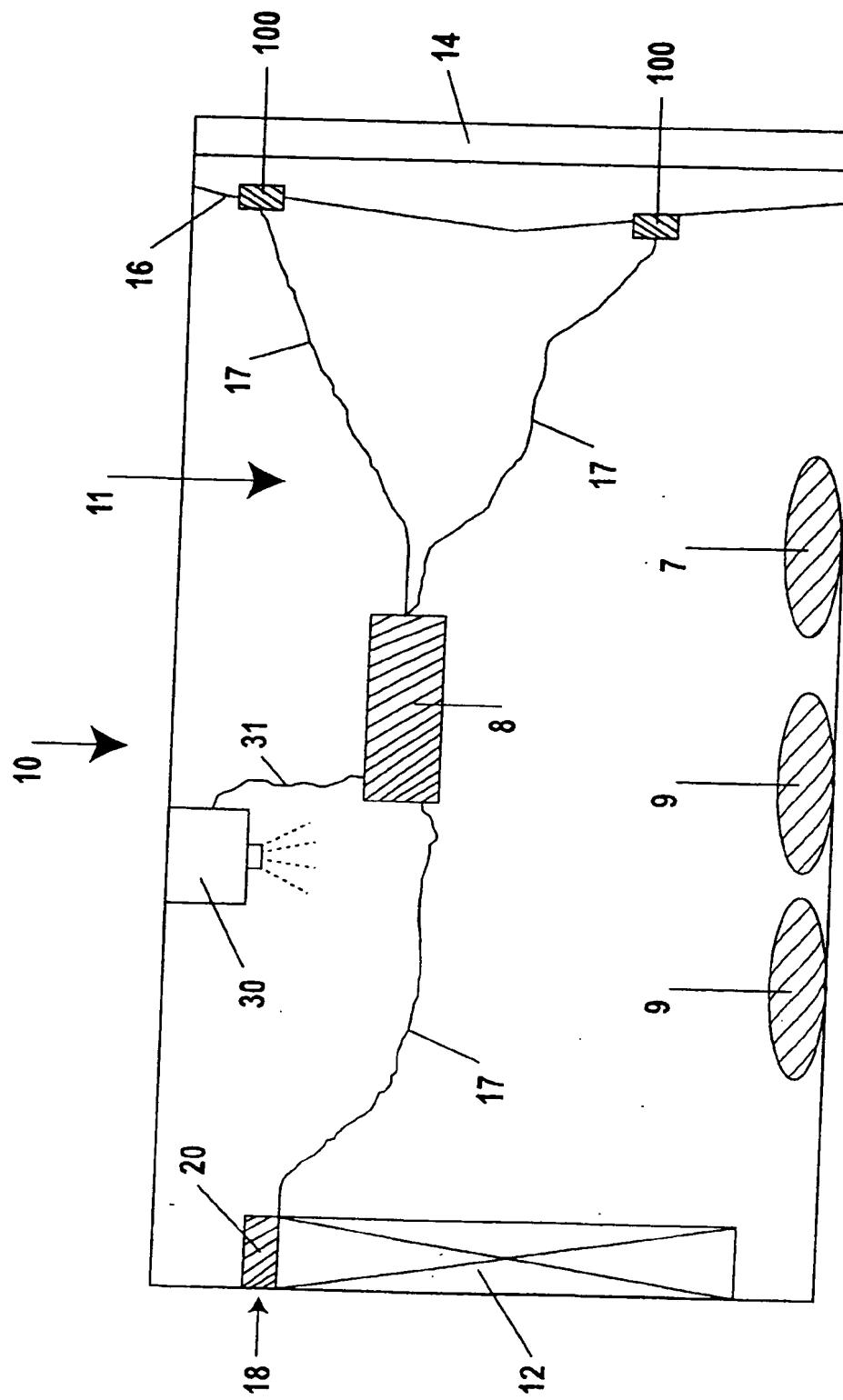
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Figure 1

A.	CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]:   B65D 81/24, 85/50, 88/74, A23L 3/3418, A23B 7/148

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
REFER ELECTRONIC DATA BASE CONSULTED BELOW

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI IPC B65D 81/-, 88/-, 90/-, 85/-, B65B 31/-, 55/18, A23L 3/34-, A01M 13/00 & keywords: ATMOSPHERE, OXYGEN, CONTAINER, CHAMBER, CONTROL, REGULATE, SENSE, VARY, MODIFY, ADMIT, FLUSH, INTRODUCE, CARBON DIOXIDE, INSECTICIDE, NITROGEN, SETPOINT, AMOUNT, LEVEL and similar terms

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/23350 A (MITSUBISHI AUSTRALIA LTD) 27 April 2000 See whole document - Substance is a purge gas	1-3, 5, 6, 8-12, 27, 29-33, 35-39
Y	See whole document	3, 5, 6, 12, 24, 27-30
X	WO 91/11913 A (THE BROKEN HILL PROPRIETARY COMPANY LIMITED) 22 August 1991 See whole document	1-3, 5, 6, 8-12, 27, 29-33, 35-39

[X]	Further documents are listed in the continuation of Box C	[X]	See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 February 2002	1 9 FEB 2002

Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	ADRIANO GIACOBETTI Telephone No : (02) 6283 2579
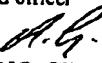
International application No.

PCT/AU01/01431

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP 136042 B1 (TRANSFRESH CORPORATION) 8 January 1992 See whole document - Nitrogen / carbon dioxide as purge gas See whole document	1, 2, 8-11, 14-23, 25-33, 35-39 3, 5, 6, 12, 24, 27-30
X Y	US 5799495 A (GAST, JR et al.) 1 September 1998 See whole document - Abstract & column 4, lines 32-47 See whole document	1, 2, 9-11, 25-27, 29-33, 35-39 3, 12
Y	AU 60062/90 A (LINDE AKTIENGESELLSCHAFT) 14 February 1991 See whole document - Page 1a, lines 4-22	27-30

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU01/01431

Box I	Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos :

   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos :

   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos :

   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II	Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

   See supplemental sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest   ☐ The additional search fees were accompanied by the applicant's protest.

   ☒ No protest accompanied the payment of additional search fees.

Supplemental Box
(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: II

The international application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept. In coming to this conclusion the International Searching Authority has found that there are different inventions as follows:

1.   Claims 1-35 relate to methods and an apparatus for introducing at least one substance into an atmosphere within a chamber and adjusting the chamber atmosphere such that the concentration of the substance does not substantially exceed a predetermined amount or is maintained at a desired constant concentration level. The methods (and associated apparatus) comprise:
(a) maintaining the oxygen concentration level in the chamber atmosphere substantially at a predetermined oxygen setpoint by (i) monitoring the oxygen concentration in the chamber, (ii) admitting into the chamber an input containing oxygen in known proportion so that the amount of oxygen in the chamber increases, and (iii) causing or permitting chamber atmosphere to exit the chamber (NB Item (iii) not a feature of the apparatus of claim 35);
(b) removing oxygen from the chamber atmosphere at a rate sufficient to require continual admission of the input into the chamber to maintain the oxygen concentration in the chamber atmosphere substantially at the set point;
(c) introducing a substance into the chamber atmosphere substantially at a predetermined substance introduction rate such that the concentration of the substance in the chamber does not substantially exceed a predetermined amount.
It is considered that the combination of features defining the method above comprises a first "special technical feature".

2.   Claims 36 to 39 also relate to an apparatus and method for introducing a substance into an atmosphere of a chamber. The apparatus comprises a substance introduction means for introducing a substance into the chamber atmosphere; and a controller with an oxygen concentration sensor for measuring the oxygen concentration in the chamber atmosphere and a control means responsive to the oxygen sensor to either (i) vary the substance introduction rate so that the concentration of the substance does not exceed a predetermined amount, or (ii) admit into the chamber an input containing oxygen when the oxygen concentration has fallen below a predetermined setpoint while introducing the substance at a constant rate. It is considered that the particular features of the apparatus, and related method, comprises a second "special technical feature".

These groups of claims are not so linked as to form a single general inventive concept, that is, they do not have any common inventive features, which define a contribution over the prior art. The common concept linking together these groups of claims is introducing a substance into a chamber atmosphere while maintaining the oxygen concentration in the chamber atmosphere at a predetermined setpoint. However this concept is not novel in the light of the following selection of prior art documents:

(D1) WO 00/23350 A (MITSUBISHI AUSTRALIA LTD)
(D2) WO 91/11913 A (THE BROKEN HILL PROPRIETARY COMPANY LIMITED)
(D3) FR 2595583 A (SOCAR)

These documents disclose a system or process where a purging gas or another gas (other than oxygen) is introduced into a chamber atmosphere. The system has oxygen sensors and control means to monitor and regulate the oxygen concentration levels in the chamber atmosphere. As such the common concept is not novel in light of these documents. Therefore these claims lack unity a posteriori.

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member						
WO	200023350	AU	200011406	EP	1175353				
WO	9111913	AU	73215/91	NZ	237105		ZA	9101070	
EP	136042	AU	32431/84	JP	61025443	NZ	205453		
		US	4642996	US	4716739	ZA	8406661		
US	5799495	NONE							
AU	60062/90	EP	412471	DE	3926194				

END OF ANNEX